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MATERIALS RESEARCH AT STANFORD UNIVERSITY

Stanford University

Prepared for:

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National Institutes of Health
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July 1975

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Fourteenth Annual Report

on

MATERIALS RESEARCH

AT

STANFORD UNIVERSITY

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CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

Fourteenth Annual Report

on

MATERIALS RESEARCH AT STANFORD UNIVERSITY

Information concerning research activities related to the science of materials during the period July 1, 1974 through June 30, 1975.

This research was supported primarily by one or more of the following agencies of the United States Government:

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July 1975

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SECTION A

INTRODUCTION

This Fourteenth Annual Report includes information briefly describing the total research activity related to the science of materials at Stanford University during the period July 1, 1974, through June 30, 1975.

This report contains brief descriptions of the various individual research programs active during the period July 1974, through June 1975. The organization of such a large and varied compilation presents a serious problem. Many programs are cooperative and involve several faculty members, and there are many faculty members with catholic interests, so that arrangement by subject area becomes cumbersome. It was decided that the simplest and most straightforward way to encompass Stanford's broad activities in this area would be an alphabetical arrangement by principal investigator. In addition to brief abstracts relating to the various research programs, compilations are included of publications, doctoral dissertations, faculty and senior staff members, research associates, graduate students and degrees awarded. Finally a name index has been added for convenience in locating references to the activities of specific individuals. From this compilation, it can be seen that research on materials and related problems is being conducted within twelve different academic departments as well as in the Hansen Microwave Laboratory.

The research described herein received financial support from many different sources. As indicated in their descriptions, some of the research programs were supported by private sources. However, most received support from one or more of the following agencies of the United States Government.

Atomic Energy Commission
Defense Advanced Research Projects Agency
Department of the Air Force
Department of the Army
Department of Commerce
Department of Health, Education and Welfare
Department of the Interior
Department of the Navy
Department of Transportation
Energy Research and Development Agency
Environmental Protection Agency
National Aeronautics and Space Administration
National Bureau of Standards
National Science Foundation

In addition to the direct support of individual research programs by the agencies mentioned above, broad-base core support was furnished by the National Science Foundation through its Materials Research Laboratory (MRL) Program under Grant No. DMR 72-03022 (formerly GH-33630), administered by the Center for Materials Research (CMR), during this past year. Prior to July 1972, this core support was provided by the Advanced Research Projects Agency through its Interdisciplinary Laboratory (IDL) Program.

Besides contributing to the direct support of many individual materials research programs, core funds from this source have been used to help pay the capital costs of some of the laboratory and office space in the McCullough Building. Also of particular importance has been the financial assistance received through these programs for the establishment and operation of a group of vital Central Facilities, which provide a truly unique service to the whole materials research community at the University.

SECTION B

MATERIALS RESEARCH PROGRAMS

1. ELASTIC AND THERMAL PROPERTIES OF COMPOSITE MATERIALS

Ardreas Acrivos, Professor of Chemical Engineering

Graduate Students:

H. -S. Chen
F. A. Gadala-Maria
M. J. Hommel
T. S. Lo
S. Moosman
J. P. Muth
G. G. Poe*
R. W. Watkins
G. K. Youngren

*Received Ph. D. during report period.

Agency Support:

NSF GK 36515X and GK 43608
NSF GK 41781
EPRI-RP-314-1

Technical Objective:

To develop a theory (substantiated by experiments) for predicting the bulk elastic and thermal properties of composite materials containing dissimilar constituents. Specifically, the aim is to investigate in detail those cases in which the addition of relatively small amounts of a suitably chosen foreign substance can alter substantially parameters such as the effective bulk elastic modulus and the effective thermal conductivity of a simple solid both at steady-state and during the transient regime, as well as to study concentrated composites in which there exists a strong interaction among the individual elements comprising the dispersed phase. The ultimate objective of this work is to provide a rational basis for designing composite materials having desired elastic and thermal properties, e.g., composites having high tensile strength but low weight, or composites which are high conductors of heat in one direction, but act as insulators in the other.

Research Report:

(1) Elastic Properties of Composite Materials Containing Solid Spheres

Graduate Student: H.-S. Chen

A theory has been developed for predicting the effective elastic moduli of composite materials containing small solid spheres in moderate concentrations. This was achieved by applying a technique recently described by Jeffrey for the analogous heat conduction problem. Experiments are being performed to test the theoretical predictions in the more dilute range and to provide much needed data for extending the theory to the concentrated regime.

(2) Thermal Properties of Composite Materials Containing Slender Inclusions

Graduate Student: H.-S. Chen

The electric conductivity of dilute suspensions of highly conducting and aligned slender fibers was studied experimentally as a model for the analogous phenomenon of heat conduction in a composite containing slender inclusions of very high conductivity. The data was found to agree, in the infinitely dilute range, with a theoretical expression recently derived by Rocha and Acrivos. A theory was developed to account for the experimental observations at higher concentrations which exhibited a very marked increase in the longitudinal effective conductivity upon the addition to the sample of small quantities of slender fibers. An attempt is now being made to extend the theory to substantially higher concentrations in which a strong interaction exists among the fibers comprising the suspension.

Reference Publications:

1. A. Rocha and A. Acrivos, "On the Effective Thermal Conductivity of Dilute Dispersions. General Theory for Inclusions of Arbitrary Shape." Q. J. Mech. Appl. Math. 26, 217 (1973).

2. W. B. Russel, "On the Effective Moduli of Composite Materials: Effects of Fiber Length and Geometry at Dilute Concentrations," J. Appl. Math Phys. (ZAMP) 24, 581 (1973).

3. A. Rocha and A. Acrivos, "On the Effective Thermal Conductivity of Dilute Dispersions. Highly Conducting Inclusions of Arbitrary Shape," Q. J. Mech. Appl. Math. 26, 441 (1973).

4. W. B. Russel and A. Acrivos, "On the Effective Moduli of Composite Materials: Experimental Study of Chopped-Fiber Reinforcement," J. Appl. Math Phys. (ZAMP) 24, 838 (1973).

5. A. Rocha and A. Acrivos, "Experiments on the Effective Conductivity of Dilute Dispersions Containing Highly Conducting Slender Inclusions," Proc. Roy. Soc. London A 337, 123 (1974).

2. CHEMICAL METALLURGY

R. N. Anderson, Associate Professor, Applied Earth Sciences

Professional Associates:

T. J. Connolly, Professor, Mechanical Engineering
W. C. Luth, Associate Professor, Geology
R. H. Jahns, Professor, Geology
G. A. Parks, Professor, Applied Earth Sciences
N. A. D. Parlee, Professor, Applied Earth Sciences

Consultants:

R. W. Bartlett, Kennecott Copper Corp., Salt Lake City
D. Cubicciotti, SRI, Menlo Park
C. A. Eckert, University of Illinois, Champaign-Urbana
K. S. Sree Harsha, San Jose State University

Graduate Students:

G. E. Beckstead
T. H. Chin
B. H. Coyle**
M. Hassan
H. H. Haung
C. D. Heising
A. Jayarajan
M. J. Mitchell*
M. T. Naney*
G. S. Selvaduray
B. D. Sloane**
E. L. Von Dohlen
J. R. Wang

* Received Ph.D. during report period.
** Received M.S. during report period.

Student Assistants:

C. Drury
T. Duralde
M. Fang
J. Koperski

Agency Support

NSF through CMR
NSF GA 35621
Bureau of Mines GA 133080
Bureau of Mines GA 133085
Stanford Institute for Energy Studies
Argonne National Lab. ANL-31-109-3100 (ERDA)

Technical Objective:

To investigate the thermodynamic, kinetic, and transport phenomena necessary for the development and design of mineral and metallurgical extraction processes.

Approach:

The approach varies with each study.

Research Report:

(1) Recovery of Non-Ferrous Metals from Auto Shredder Refuse

Professional Associates: G. A. Parks

Graduate Student: B. H. Coyle

The objectives of this research program are to develop a hydrometallurgical method of producing pure zinc, copper and aluminum metals from the nonmagnetic metallic scrap generated by junk automobile shredding operations. An optimum hydrometallurgical circuit has been designed and the economic analysis of a 250 ton/day plant is proceeding. The chemical kinetics of the hydrometallurgical operations in the process are being evaluated in the laboratory.

(2) Equilibrium Vapor Pressure Study of Bi_2S_3

Consultants: R. W. Bartlett
D. Cubicciotti

Graduate Student: M. J. Mitchell

Mass spectrometric and thermogravimetric Knudsen effusion vaporization studies of sulfide have been performed to determine the species present in the vapor at temperatures up to the melting point of the sulfide. These basic thermodynamic data for trace elements in minerals are necessary for such geochemical applications as prospecting and developing new extractive metallurgical techniques. Sublimation enthalpies and entropies were determined for synthetic bismuthinite (Bi_2S_3). Contrary to previous work, the Bi_2S_3 appears to sublime congruently in the same manner as that found for Sb_2S_3 and

As_2S_3.

(3) Pollution-Free Copper Extraction Metallurgy

Consultant: R. W. Bartlett

Graduate Student: H. H. Haung

A mixed lime-concentrate pellet roast process has been developed for the metallurgical treatment of copper sulfide floatation concentrates. Air pollution by SO_2 is practically eliminated since all sulfur is retained as a solid with the lime. The oxidized copper in the pellet can be dissolved in a sulfuric acid leach and recovered as cathode copper. The critical parameter in this process is the roasting temperature -- temperatures that are too high produce insoluble copper-ferrite and temperatures that are too low produce acid soluble iron sulfate. Studies of the operation of the process in a fluidized bed are currently underway.

(4) Analysis of an On-Stream Particle Size Analyzer

Consultant: R. W. Bartlett

Graduate Student: T. H. Chin

The theoretical analysis necessary to model the behavior of a new concept of on-stream particle size analysis is being developed. This analysis method is based on continuously measuring and comparing the percent solids in an internal reference stream containing only undersized particles. A semi-permeable hydraulic system is used so that the mass concentration in the internal stream can vary and is proportional to the undersize particle mass concentration in the pulp stream. The density changes in the two pulp streams are continuously measured with nuclear gauges.

(5) New Energy Systems for Process Metallurgy

Graduate Student: A. Jayarajan

The enormous energy requirements of the metals industry suggests consideration of new energy alternatives. The MHD generator seems particularly well suited to the integrated production of metals utilizing electrolytic and carbothermic reduction such as aluminum and steel. In this study, a model of a dedicated MHD facility used in making iron is investigated. This arrangement is capable of reducing the overall carbon consumption per ton of iron by 1/3. Moreover, metallurgical coke is not required in this process. Improved efficiencies are due to the additional MHD energy recovered during the combustion of coal that are normally lost in the conventional iron blast furnace.

(6) Extraction of Germanium and Gallium from Coal Furnace Flue Dust

Graduate Student: M. Hassan

Gallium and Germanium, among other minerals, are found in coal and concentrated in the flue dust upon combustion. Hydrometallurgical recovery by leaching the flue dust to recover these materials is uneconomical. This research program has studied the behavior of these elements during combustion using a knudsen effusion mass spectrometer to identify the vapor species and its characteristics. Based on this study, an economical process using high temperature metallurgy is being designed to recover the trace mineral content of coal.

(7) The Chemistry and Physical Mechanics of Nuclear Wastes in Rocks

Professional Associates:	T. J. Connolly R. H. Jahns W. C. Luth
Graduate Students:	C. D. Heising M. T. Naney B. D. Sloane E. L. Von Dohlen

This study is examining the magma creation in rock systems (basaltic and granitic) as functions of temperature and time. Simulated high level nuclear waste in calcined form is being used to relate the experimental rock-waste interaction to the engineering requirements and safety aspects of high-level radioactive waste disposal in these host rocks. Deep rock disposal appears to be a viable method for the ultimate disposal of nuclear waste. The methods of the nuclear waste re-entering the biosphere by magma flow and by leaching of the material are being studied as well as the behavior of typical container materials suggested for use in this application.

(8) Recovery of Zirconium from Zircalloy Cladding (Hulls) from Spent Nuclear Reactor Fuel Rods and Disposal of Clinging Nuclear Wastes

Professional Associate: N. A. D. Parlee (Co-director)

Graduate Students: G. S. Selvaduray
J. R. Wang

This study is directed towards developing a high temperature metallurgical process for recovering and recycling the nuclear grade zirconium used as fuel rod cladding in light water nuclear reactors. The current practice is to chop the fuel rods and leach the fuel oxide in the fuel reprocessing plant and discard the zirconium hulls. The approach in this study is to dissolve the zirconium in a molten solvent metal and precipitate the zirconium free of contamination by forming the stable nitride phase. The purified ZrN can then be separated and converted to the metal for reuse by several techniques. Initially, this study is concerned with examination of the solution characteristics of zirconium in selected metal solvents, and with the nitrogen-nitride reaction kinetics and equilibria for the reaction

$$\underline{Zr}(\text{dissolved}) + 1/2\ N_2(g) = ZrN(s)$$

(9) Associated with Professor N. A. D. Parlee on the following: Nitrogen Nitride Reactions in Liquid Uranium Alloys and Their Applications to the Reprocessing of Nuclear Reactor Fuels

Graduate Student: K. W. Au

Carbothermic and Carbo-Nitrothermic Reduction of Reactive Metal Oxides in Metal Solvents

Graduate Student: N. Bakshani

Reference Publications:

1. T. G. Schicks, R. N. Anderson and N. A. D. Parlee, "Kinetics of Nitride-Forming Reactions in Liquid Uranium-Tin Alloys," Abstr. Bull. of Met. Soc. AIME, Feb. 1974 Annual Meeting, J. High Temp. Sci. 6, 351-368 (1974).
2. A. Fuwa, R. N. Anderson, and N. A. D. Parlee, "Nitrogen-Nitride Equilibria in Liquid Pr-Sn, Gd-Sn and U-Pr-Gd-Sn Alloys and Their Application to the Reprocessing of Nuclear Fuels," Abstr. Bull. of Met. Soc. AIME, Feb. 1974 Annual Meeting. Accepted for pub. J. High Temp. Sci. 1975.
3. A. Fuwa, R. N. Anderson and N. A. D. Parlee, "Nitrogen-Nitride Equilibria in Y-Sn Alloys," J. High Temp. Sci., 6 259-266 (1974).
4. M. Rao, M. Mitchell, and R. N. Anderson, "Study of Inter-diffusion in Electroplated Sn-Ni on Au," Solid State Technology, Nov. 1974.
5. R. N. Anderson, N. A. D. Parlee and A. Fuwa, "Separation of Fission Product Metals from Spent Uranium Fuels by Nitriding," Abstr. Bull., Trans. American Nuclear Soc., Winter Meeting, Oct. 1974.
6. R. N. Anderson, and N. A. D. Parlee, "Applications of Solution Thermodynamics in High Temperature Metallurgical Processes," Abstr. Bull. of Annula A.I.Ch.E. Meeting, Dec. 1974.
7. M. Mitchell and R. N. Anderson, "Equilibrium Vapor Pressure Study of Bi_2S_3," Abstr. Bull of A.I.M.E. Annual Meeting, Feb. 1975.

3. ACOUSTIC WAVES AND DEVICES

B. A. Auld, Adjunct Professor, Hansen Laboratories

Graduate Students:

S. A. Farnow
J. G. Harris

Agency Support:

Navy N00014-75-C-0359
Navy N00014-75-C-0632
NSF GK 43143

Technical Objective:

To obtain an understanding of acoustic field theory and to apply the basic principles to device development

Research Report:

(1) Acoustic Fresnel Zone Plates (S. A. Farnow and B. A. Auld)

Acoustic zone plate transducers have been constructed to focus sound in water at frequencies near 10 MHz. Photolithographic techniques were used to evaporate gold zone plates (of ten zones) as electrodes on one face of PZT-5A discs, with the opposite face being given a full-face electrode. Focal plane intensity distributions with half widths of 0.22 mm or 1.5 wavelengths have been achieved. An improvement is realized by a poling technique which alternates the polarization of the ceramic in adjacent zones. In this way, the zone plate may be converted to a phase plate, resulting in, among other improvements, a 4-fold increase in the intensity at the focus.

Acoustic imaging has been performed with these transducers in both transmission and reflection modes. In both cases, the object is mechanically scanned in a water bath in the focal plane of the transducer(s). In the transmission system, the object is insonified from one side with a phase plate transducer. The transmitted sound is then detected from the other side with a second phase plate transducer. A single phase plate transducer is used for reflection imaging, with the system operating in a pulse-echo mode. Resolutions of 1.8 wavelengths have been achieved.

(2) Acoustic Waveguide and Scattering Studies (J. G. Harris, J. Souquet, A. Rønnekleiv, H. J. Shaw and B. A. Auld)

The aims of this program are to analyze the waveguide modes in surface acoustic wave systems, to study scattering of acoustic surface waves by obstacles, to arrive at useful analytic techniques which would be applicable to a large class of surface acoustic wave problems, and to carry out experimental tests of the theory. For these purposes, we have been examining variational techniques and have developed these techniques for application to problems of the above kinds.

This work is aimed at studying certain problems involving the propagation, guiding and scattering of surface acoustic waves. Waveguides provide high packing density for information storage and processing in surface acoustic wave devices. Scattering from slots is useful for devices in which we convert surface acoustic waves to bulk acoustic waves and vice versa, and in dispersive surface acoustic wave delay line filters.

We have recently carried out experimental measurements of the scattering of surface acoustic waves into bulk acoustic waves at a single groove, using bulk wave transducers which allow measurement of the polar radiation pattern of the bulk waves, and also measurements of the bulk wave scattering by periodic arrays of grooves. These measurements have been carried out at frequencies in the 1 MHz range, using rectangular grooves and V-grooves machined in aluminum surfaces. We have calculated the theoretical scattering characteristics of these grooves. As might be expected, the bulk wave radiation from a groove in an infinite array is quite different from that of a single isolated groove. Good agreement has been obtained between the theoretical computations and the measured results.

Reference Publications:

1. B. A. Auld and S. A. Farnow, "Coupling of Surface and Volume Acoustic Waves by a Photoconductive Grating," J. Appl. Phys. 45, 4315 (1974).

2. B. A. Auld, M. E. Drake, and C. G. Roberts, "Monolithic Acoustic Imaging Transducer Structures with High Spatial Resolution," Appl. Phys. Letters 25, 478 (1974).

3. S. A. Farnow and B. A. Auld, "Acoustic Fresnel Zone Plate Transducers," Appl. Physics Letters 25, 681 (1974).

4. S. A. Farnow and B. A. Auld, "An Acoustic Phase Plate Imaging Device," presented at the 6th International Symposium on Acoustical Holography and Imaging to be published in Acoustical Holography, Vol. 6 (Plenum Press).

4. CONTINUUM THEORY OF LATTICE DEFECTS, FRACTURE, AND SURFACE WAVES IN ANISOTROPIC MEDIA.

D. M. Barnett, Associate Professor, Materials Science & Engineering and Applied Mechanics

Graduate Students:

S. D. Gavazza
W. H. McConnell
J. G. Slater
E. Olsen

Post-doctoral Research Associate

Dr. Y. Rajapakse

Agency Support:

NSF through CMR
NASA NGR 662

Technical Objectives:

(1) To produce new straightforward methods for studying the effects of elastic anisotropy on static and dynamic fracture mechanics, on the elastic fields of inclusions, dislocations, and point defects, and on surface wave and other steady state wave propagation.

(2) To produce efficient computer schemes for generating diffraction contrast patterns for defect identification.

(3) To study applications of singular dislocation theory to the modelling of geophysical phenomena.

1. Forces on Dislocations

Graduate Student: S. D. Gavazza

The proper definition of the self-force on a dislocation loop tending to move arbitrarily in its plane has been achieved, thus reconciling a difficulty which had lain unresolved in the literature for more than a decade. A unified treatment of energy release rates associated with lattice defects has been developed within the same framework.

2. Effective Elastic Moduli of Deformable Heterogeneous Solids

Graduate Student: W. H. McConnell

A rigorous analysis has been developed to show how the macroscopic elastic response of a heterogeneous solid (composite medium of polycrystalline medium) may be obtained by replacing the real discontinuous elastic moduli by simpler "effective elastic constants".

3. Defect Identification using Computer Simulation

Graduate Student: W. H. McConnell

A new method has been proposed for numerically integrating the Howie-Whelan Equations to produce computed electron micrographs of diffraction contrast from 2-D and 3-D lattice defects.

4. Singular Dislocation Theory Applied to Geophysical Phenomena

Faculty: D. M. Barnett, L. B. Freund (Visiting), A. Nur

An appropriate dislocation model of a vertical strike-slip fault has been used to predict fault friction stress in terms of measured surface displacement data. An investigation of viscous creep beneath a crustal fault is currently in progress.

5. Surface Waves in Piezoelectric Media

(with Professor Jens Lothe, Oslo University, Oslo, Norway)

A new method for numerically studying piezoelectric surface waves has been developed based on prior results obtained for ordinary Rayleigh waves in elastically anisotropic media. The method is also being applied to Stoneley waves and Love waves in anisotropic layered media.

Reference Publications:

1. D. M. Barnett and J. Lothe, Consideration of the Existence of Surface Wave (Rayleigh Wave) Solutions in Anisotropic Elastic Crystals, J. Phys. F: Metal Physics, 4, 671 (1974).

2. R. J. Asaro and D. M. Barnett, On some Three-Dimensional Dislocation Problems in Anisotropic Media, J. Phys. F: Metal Physics, 4, L103 (1974).

3. S. D. Gavazza and D. M. Barnett, The Elastic Interaction between a Screw Dislocation and a Spherical Inclusion, Int. J. Eng'g. Sci., 12, 1025 (1974).

4. D. M. Barnett and J. Lothe, An Image Force Theorem for Dislocation in Anisotropic Bi-Crystals, J. Phys. F: Metal Physics, 4, 1618 (1974).

5. R. J. Asaro and D. M. Barnett, The Non-Uniform Transformation Strain Problem for an Anisotropic Ellipsoidal Inclusion, J. Mech. Phys. Solids, 23, 77 (1975).

6. D. M. Barnett, J. K. Lee, H. I. Aaronson, and K. C. Russell, The Strain Energy of a Coherent Ellispoidal Precipitate, Scripta Met., 8, 1447 (1974).

7. D. M. Barnett and J. Lothe, Dislocations and Line Charges in Piezoelectric Insulators, Phys. Stat. Solidi, 67, 105 (1975).

8. J. Lothe, R. J. Asaro, D. M. Barnett, and J. P. Hirth, Comments on the Indenbom-Alshits Theory for Dislocations in Anisotropic Media, Phys. Stat. Solidi (b), 66, K79 (1974).

9. W. R. Delameter, G. Herrmann, and D. M. Barnett, Weakening of an Elastic Solid by a Rectangular Array of Cracks, J. Appl. Mechanics, 42, 1, 74 (1975).

10. D. M. Barnett and J. Lothe, Line Force Loadings on Anisotropic Half-Spaces and Wedges, Physica Norvegica (in press).

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5. STRUCTURAL AND MECHANICAL PROPERTIES OF MATERIALS

C. R. Barrett, Associate Professor, Materials Science and Engineering

Graduate Students:

K. S. Majumder
P. P. Pizzo

Agency Support:

AFOSR 73 2434 A
NSF GH 40770
AT (04-3) 326 PA 17

Technical Objective:

To obtain an understanding of the structure-property relationships associated with the mechanical properties of crystalline materials.

Approach:

Materials with unique microstructural parameters are being prepared and tested to determine the influence of structural features such as grain size, dispersoid distribution, and inhomogeneous precipitate distribution, on mechanical properties of metallic alloys.

(1) High Rate Physical Vapor Deposition Studies

Graduate Student: K. S. Majumder

A fundamental research program is underway to study the structure and properties of dispersion hardened copper and nickel base alloys. One unique aspect of this research program is that the preparation of the composites is via physical vapor deposition. This technique of preparation has several aspects which differ greatly from conventional preparation techniques and is capable of producing composite material with microstructures ideal for high temperature creep resistance. The systems chosen for study include $Cu\text{-}Al_2O_3$ and pure Ni and Ni-Cr alloys with dispersions of Al_2O_3 and Y_2O_3.

(2) Influence of Precipitate Free Zones on the Mechanical Behavior of Precipitation Hardened Alloys

Graduate Student: P. P. Pizzo

A study is underway to determine the influence of precipitate free zones on high and low temperature strength in precipitation hardened aluminum alloys (Al-Zn-Mg). Areas of special interest include grain boundary sliding, high temperature creep strength and fracture initiation. Results to date suggest that the precipitate free zones adjacent to grain boundaries do not directly effect the strength or ductility of aluminum alloys. An indirect effect has been observed however, in which the heat treatments used to produce precipitate free zones of different size results in slight variations in matrix strength with a resultant variation in observed mechanical properties.

Reference Publications:

1. R. G. Stang, W. D. Nix and C. R. Barrett, "The Influence of Subgrain Boundaries on the Rate Controlling Creep Processes in Fe-3% Si", accepted for publication in Met. Trans.
2. A. E. Geckinli and C. R. Barrett, "Superplastic Deformation of the Pb-Sn Eutectic", accepted for publication in Met. Trans.
3. C. R. Barrett, "Method of Employing Aluminum Anodization to Fabricate Single and Double Layer Metallization on Integrated Circuits", U.S. Patent Application.

6. PHOTOELECTRONIC MATERIALS PHYSICS

Clayton W. Bates, Jr., Associate Professor
Materials Science and Engineering and Electrical Engineering

Professional Associates:

- R. Morwood*
- C. Robbins*
- H. Greenstein - Visiting Scholar
- W. Proctor - Visiting Scholar

*with Varian Associates

Graduate Students:

- D. Das-Gupta
- L. Galan
- O. L. Hsu
- A. McHale
- A. M. Salau
- N. H. Tsai

Agency Support:

ARPA through CMR
Army Research Office (Durham) DAHC-04-73C-0003
NASA NGR 05-020-710

Technical Objectives:

To investigate the structural, electronic and optical properties of crystalline and amorphous photoelectronic materials in an effort to understand the underlying phenomena with the aim of using these materials in photoelectronic imaging devices such as low light level sensing systems, photomultiplier tubes, etc. and for use in x-ray image intensification and detection applications such as diagnostic radiology. This investigation has been expanded to include the interaction of intense radiation fields with matter.

Approach:

Since the approach to each system investigated will depend upon the use that the system will be put to in a particular device or system, each system will be approached differently and is described accordingly.

Research Report:

(1) Line-width and Tuning Effects in Resonant Excitation

Professional Associate: H. Greenstein

Effects deriving from the finite spectral line width of an irradiation source are investigated for the resonant excitation process and found to be of particular interest when the irradiation spectral width is comparable with atomic (or molecular) line widths. An application of high current interest is laser isotope separation using relatively broad band but tunable dye lasers for selective excitation. Expressions are derived in systematic fashion for the absorption coefficient and for the yield, taking into account three independent line shapes - the first describing the irradiation source, the other two describing Lorentz and Doppler broadening of the atomic (or molecular) medium. Saturation effects are included, but propagation effects are neglected. It is shown that the customary distinction between homogeneous and inhomogeneous atomic-line broadening must be modified if the irradiation is not monochromatic. A further result of practical importance is that there exists an optimum irradiation line width that maximizes the yield for resonant transfer. In this respect, the relatively broad spectral widths characteristic of dye lasers are to be regarded as an advantageous feature, contrary to what is generally assumed.

(2) Optical Properties of CsI(Na) and Heat-Treated Pure CsI

Graduate Students: O. L. Hsu
A. M. Salau

This work is an extension of last year's work on absorption, excitation and emission spectra of CsI(Na) and CsI. On the basis of the similarity of luminescence properties of CsI(Na) crystals and heat-treated crystals of pure CsI excited in the long wavelength tail of the fundamental absorption, the effect of sodium in CsI(Na) is tentatively explained. This work has been written up and accepted for publication in Physics Letters A.

(3) Strain-Induced Room Temperature Photoluminescence in CsI and CsI(Na)

This work is a continuation of last year's work on the observation of luminescence from strained specimens of CsI(Na) and CsI. We have found that producing strains by deforming the specimen (4% deformation) produces luminescence at 425nm in pure CsI at room temperature which was not present before and increases the luminescence in samples of CsI(Na) at room temperature which does not contain the optimum amount of sodium for maximum luminescence at 425nm. Deforming (4%) samples of CsI(Na) with the optimum amount of sodium (6ppm) produces no change in the emission at 425nm at room temperature.

At present these results are not clearly understood. The 425nm emission strongly resembles the thermoluminescence produced at low temperatures and attributed to the migration of V_k centers followed by the radiative recombination with electrons trapped at sodium sites. However, it is uncertain both why the intensity of the emission at room temperature decreases for $\overset{+}{Na}$ concentrations in excess of 6ppm or why deformation (or thermal quenching) has such a pronounced effect on the intensity unless these treatments have a dissolution effect on sodium or other structural clusters already present in the lattice. Yet another possibility is that the deformation (or thermal) treatments may so substantially increase the mobility of the irradiation produced V_k centers that even the trace amounts $\overset{+}{Na}$ present in the crystal are now quite effective as recombination sites. A more detailed investigation now underway hopefully will shed some light on this matter. These results have been accepted for publication in Solid-State Communications.

(4) Luminescence Phenomena in CsI(Na)

Graduate Student: O. L. Hsu

Absorption, emission and excitation spectra of CsI(Na) were measured on bulk single crystals and thin films at room and liquid nitrogen temperatures. Excitonic absorption peaks as well as absorption in the long wavelength tail of the fundamental absorption which is not present in pure CsI were observed. In addition to emission at

4250Å, excitonic emission at 3400Å normally found at LNT has also been observed at RT. This room temperature UV emission is closely related to the heat treatment process that the specimen received.

Work is presently underway to extend our measurements from above room temperature (70°C) continuously down to liquid helium temperature. In this manner we will be able to study the temperature dependence of all quantities measured previously, i.e., emission, excitation and absorption, over a wide temperature range. These studies will be particularly important for revealing the character of the absorption in the long wavelength tail of the fundamental absorption which is not present in pure CsI. In addition to these measurements, polarization studies will also be made to determine, if possible, the symmetry of the luminescent centers and the association of the sodium ions with these centers. This work has been written up and submitted to the Journal of Luminescence.

(5) Luminescence Phenomena in CsI

Graduate Student: A. Salau

The photoluminescence of unactivated thin films and bulk single crystals of CsI excited by UV-radiation was investigated as the temperature was cycled from room temperature to liquid nitrogen temperature (LNT) back to room temperature. In addition to the low temperature luminescence at LNT, we observed ultra-violet luminescence and both blue and yellow luminescence in the thin films and bulk single crystals of CsI respectively for edge excitations (235nm) when the samples warmed back to room temperature after they had been cooled to LNT. We tentatively ascribed this room temperature after cooled luminescence (RTAC) to electron-hole recombination at some imperfections or structural lattice defects (probably of the vacancy type) created by cooling and irradiation with nonionizing UV radiation at LNT. This RTAC luminescence is reported here for the first time. This work has also been submitted to the Journal of Luminescence.

(6) Two-Photon Spectroscopy in Alkali Halides

Graduate Student: L. Galan

This work is still in a preliminary stage. The method of two-photon spectroscopy will be used in an attempt to determine the site symmetry of nonisomorphic impurities in alkali halides responsible for luminescence in these materials.

(7) Devitrification Studies of High Purity Silica Fibers

Graduate Student: Anna McHale

A program of research and development which hopefully will lead to the basic physical understanding of devitrification of high purity silica fibers which are used in reusable surface insulation (RSI) has been started. Our main efforts will be directed towards investigating devitrification of these fibers as a function of temperature and time and impurity content. The principal technique employed will be that of x-ray diffraction, though other techniques such as ESCA (x-ray photo-emission) and EPR (electron paramagnetic resonance) will be explored as possible approaches for supplying complementary and additional information to the devitrification process.

Our initial efforts employing x-ray diffraction have been most promising. Some experiments employing ESCA have been done with somewhat ambiguous results. Work using both of these techniques will continue.

(8) New Trends in X-ray Image Intensification

We have designed and constructed an experimental 210mm input 70mm fibre-optic output x-ray image intensifier tube for diagnostic radiology. The tube has a $\mathrm{CsI(Na)}$ input scintillator and a computer designed electron-optical system. From measurements of the modulation transfer function (MTF) of this 3:1 minification tube, it is apparent that a tube with a 17" input and a 4" (100mm) output from which 100mm contact prints may be made, will be superior to par screen-film combinations as regards information content and reduced dosage to the patient.

Reference Publications

1. C. W. Bates, Jr., "New Trends in X-ray Image Intensification", Proc. of Society of Photo-Optical Instrumentation Engineers 47, 152 (1975).

2. C. W. Bates, Jr. and Stephen Sparks, "Modulation Transfer Function of a 210/70mm Fibre-Optic Output X-ray Image Intensifier Tube", Applied Optics Letters, July 1975.

3. C. W. Bates, Jr. et al, "Optical Properties of CsI(Na) and Heat-Treated Pure CsI", (accepted for publication in Physics Letters A).

4. C. W. Bates, Jr. et al, "Strain-Induced Room Temperature Photoluminescence in CsI and CsI(Na)", (accepted for publication in Solid-State Communications).

5. Olive Lee Hsu and C. W. Bates, Jr., "Luminescence Phenomena in CsI(Na)" (submitted to Journal of Luminescence).

6. Akinola Salau and C. W. Bates, Jr., "Luminescence Phenomena in CsI", (submitted to Journal of Luminescence).

7. H. Greenstein and C. W. Bates, Jr., "Linewidth and Tuning Effects in Resonant Excitation", Jour. Opt. Soc. 65, 33 (1975).

7. ELECTROMAGNETIC PROPERTIES OF SUPERCONDUCTORS

M. R. Beasley, Associate Professor, Applied Physics and Electrical Engineering

Professional Associates:

R. A. Klemm
J. M. Rowell

Graduate Students:

D. F. Moore
J. C. White

Agency Support:

JSEP
NSF through CMR

Technical Objectives:

To extend and deepen the understanding of the electromagnetic behavior of superconductors and superconducting structures and devices.

Approach:

The response of superconductors to currents, electric and magnetic fields, and electromagnetic radiation under a wide variety of conditions are studied and related to the basic properties, structure, material parameters, and geometry of the superconductors.

Research Reports:

(1) Layered Superconducting Compounds

A theoretical study of the upper critical field H_{c2} expected in layered compounds, carried out in collaboration with A. Luther of Harvard, has been completed. The theory was carried out using both the Josephson coupled model of Lawrence and Doniach, and also using microscopic BCS theory. The results predict that for sufficiently decoupled layers, as should occur in the intercalated compounds, H_{c2} exhibits a dimensional crossover as the temperature T is reduced below T_c. Near T_c conventional anisotropic 3-D behavior is expected but at lower temperatures, for which the GL coherence length perpendicular to the layers $\xi_z(T)$

can become smaller than the layer separation, H_{c2} behaves two dimensionally and is determined by the properties of the individual layers. It was found that the magnitude of the observed critical fields could be accounted for by Pauli paramagnetic limiting in the layers but only if the spin-orbit scattering time τ_{so} was $\sim 10^{-14}$ sec. Experiments carried out with D. Prober at Harvard show that $TaS_{1.6}Se_{0.4}(collidine)_{1/6}$ has a $dH_{c2}/dT = 240$ kOe/K, larger than that of any previously measured superconductor.

Reference Publications and Presentations:

W. E. Lawrence and S. Doniach, "Theory of Layer Structure in Superconductors," in Proc. 12th Int. Conf. on Low Temp. Phys., Kyoto, 1970.

R. A. Klemm, M. R. Beasley, and A. Luther, "The Upper Critical Field of Layered Superconductors," J. Low Temp. Phys. 16, 607 (1974).

R. A. Klemm and M. R. Beasley, "Theory of the Upper Critical Field in Layered Superconductors," Phys. Rev. (in press).

D. E. Prober, M. R. Beasley, and R. E. Schwall, "Superconducting Critical Fields of TaS_2 and $TaS_{1.6}Se_{0.4}$ Organic Intercalation Compounds," Bull. Am. Phys. Soc. 20, 342 (1975).

(2) High-K, High-T_c Superconducting Thin Films

Oxide layer tunnel junctions have been formed on Nb_3Sn thin films fabricated using dual electron beam codeposition by the Geballe group. These junctions are demonstrably superior to all known previous junctions made on Nb_3Sn. The Nb_3Sn energy gap has been measured to be 6.5 meV (or 4.2 kT_c) and relatively unobscured by extraneous quasiparticle states beneath the gap. Clear Josephson tunneling and related Fiske steps have been observed. Tunneling characteristics obtained in a parallel applied field suggest that for these films a surface barrier to fluxoid penetration exists for fields up to ~ 2500 Oe or $\sim 0.5\ H_c$ for Nb_3Sn. This implies fluxoids can be prevented from entering such films for fields up to about ten times the bulk H_{c1}.

Reference and Publication:

R. H. Hammond, "Electron Beam Evaporation Synthesis of A15 Superconducting Compounds: Accomplishments and Prospects," IEEE Trans. Mag. MAG-11, 201 (1975).

(3) High-T_c Superconducting Microbridges

Long, 2 μm wide microbridges of 0.15 μ thick Nb_3Sn thin films have been successfully fabricated using photolithography and ion beam milling. Measurements of the electrical characteristics (i.e., I-V curves) are underway.

8. STRUCTURES OF AMORPHOUS MATERIALS

A. I. Bienenstock, Professor, Materials Science & Engineering and
Applied Physics

Professional Associate:

S. C. Rowland

Graduate Students:

S. H. Hunter
S. Narasimhan*

*Received Ph.D. during report period.

Agency Support:

NSF GH40785
NSF through CMR

Technical Objectives:

To investigate the structural, thermal and crystallization properties of amorphous solids in an effort to understand the relationships among these, as well as the electronic and vibrational properties.

Approach:

The approach to each system depends on the particular system and is described accordingly.

Research Report:

(1) Extended X-ray Absorption Fine Structure (EXAFS) Studies of Amorphous Materials

Graduate Student: S. H. Hunter

During the early part of this report year, the development and testing of the experimental x-ray spectrometer facility at the Stanford Synchrotron Radiation Project for the study of EXAFS was completed. Attention was then turned to data acquisition and the refinement of data acquisition techniques. EXAFS data were obtained for crystalline and amorphous samples of Se, GeSe, As_2Se_3 and Cu-As-Se alloys.

Detailed data analysis is now underway for As_2Se_3 and GeSe.

While detailed analyses of the Cu-As-Se glasses have not been performed, it is interesting to note that the EXAFS spectra obtained from glasses of the composition $Cu_{.2}(As_{.4}Se_{.6})_{.8}$ and $Cu_{.3}(As_{.4}Se_{.6})_{.7}$ are almost identical to those obtained from $CuAsSe_2$. This result lends credence to, but does not prove, the hypothesis of Liang et al.[1] that large regions of these glasses have an atomic arrangement and composition close to that of glassy $CuAsSe_2$.

At the same time, the x-ray diffraction radial distribution functions obtained by Liang et al.,[1] for the Cu-As-Se system have been reanalyzed. It has been shown that the first neighbor peak areas can be fit to remarkable accuracy with the simple assumption that the average coordination number in the glass is 8-N, where N is the average number of electrons per atom.

(2) Structure of Glassy Tl-As-Se Alloys[2]

Graduate Student: S. Narasimhan

In last year's report, it was stated that extensive x-ray radial distribution function (RDF), differential thermal analysis (DTA) and scanning electron microscopy (SEM) studies of glassy Tl-As-Se alloys had been performed, with particular emphasis on alloys of the form $Tl_x(As_{.4}Se_{.6})_{1-x}$. The SEM studies indicated that the glasses with x=0.2 and 0.3 were phase separated, while that with x=0.05 was not. No definitive conclusion could be reached on the sample with x=0.1. During the present report period, detailed analyses of these experimental results were performed.

Most important was the development of a network modifier-network former model to deal with alloys of this form. The classical oxide models deal with alloys of two or more stoichiometric oxides. In the cases studied here, however, we are dealing with the alloy of a simple metal with a stoichiometric selenide. The generalized model, which allows for As-As bonding, yields very good agreement with experiment for the samples with x=0.05 and x=0.10. It does not fit, nor is it expected to be applicable to, the samples with x=0.20 and 0.30. In these samples, it appears as if large portions of the samples have compositions and structures which are extremely close to that of glassy $TlAsSe_2$. It is believed that the formation of these regions accounts for the large decrease in the band gap and increase in the conductivity with the addition of Tl to As_2Se_3.

(3) Structure of Germanium Chalcogenide Glasses

Professional Associate:

S. C. Rowland

Graduate Students:

S. H. Hunter
S. Narasimhan

Radial distribution function studies of samples in the Ge-Sn-S and Ge-Pb-S glass forming systems have been performed. It was anticipated, in this analysis, that the Sn and Pb would substitute for the Ge and that the difference in scattering factors between these elements and Ge might help us to distinguish various structural models. Examination of the rdf's indicated that a considerable increase in understanding of these systems could be obtained through an obtainable increase in rdf resolution. For this reason, modifications of our x-ray diffraction scanning and detecting systems were undertaken so that high statistical accuracy could be obtained at high diffraction angles. These modifications have almost been completed and new diffraction runs will soon be initiated.

Reference Publications and Presentations:

1. K. S. Liang and A. I. Bienenstock, "Structural Studies of Glassy $CuAsSe_2$ and $Cu\text{-}As_2Se_3$ Alloys", Phy. Rev. B 10 1528 (1974).
2. S. Narasimhan, "The Structure of Amorphous Alloys of Arsenic Triselenide and Thallium", Ph.D. Thesis, Stanford University, 1974.
3. K. S. Liang and A. Bienenstock, "Group II-A Impurities in Glassy As_2Se_3", J. Non-Cryst. Solids 17, 289 (1975).
4. A. Bienenstock, "Structural Characterization of Amorphous Semiconductors", Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors Garmisch-Partenkirschen, Sept., 1973. Edited by J. Stuke and W. Brenig (Taylor and Francis, London 1974).

5. G. B. Fisher, I. Lindau, B. A. Orlowski, W. E. Spicer, Y. Verhelle and H. E. Weaver, "X-ray and Ultraviolet Photoemission Studies of the Electronic Structure of the Amorphous Ge_xTe_{1-x} System", reference 4, page 621.
6. G. B. Fisher, J. Tauc and Y. Verhelle, "Vibrational Modes and Bonding in the Amorphous Ge_xTe_{1-x} System", reference 4, page 1259.

9. PROPERTIES OF ADSORBENTS AND CATALYSTS

M. Boudart, Professor, Chemical Engineering and Chemistry

Professional Associates:

J. E. Benson
V. A. Shvets

Graduate Students:

B. L. Beegle
J. A. Dumesic*
E. E. Gonzo†
Y. L. Lam
K. L. Lim
R. J. Madon*
M. L. Murtiff
D. C. Silverman
B. D. Turnham*

†Received M. S. during report period.
*Received Ph. D. during report period.

Agency Support:

NSF GP 42186
NSF GK 17451X
NSF ENC 74-22234
ARPA through CMR
Exxon Research and Engineering Company
NSF through CMR

Technical Objective:

To prepare and characterize finely divided materials and understand their chemical surface reactivity and catalytic activity in selected reactions.

Approach:

Catalysts consisting of metal particles on a porous support are prepared in such a way that the average particle size of the metal is varied between 1 and 10 nm. The number of surface metal atoms in each sample is titrated by a suitable selective chemisorption technique. Then the turnover number N, i.e., the number of molecules of a reactant transformed per surface metal atom per second is measured under selected conditions. As it is well known that metal particles in the critical size range between 1 and 10 nm exhibit different surface structures, i.e., different proportions of surface atoms with varying coordination numbers, an effect of particle size on N determines whether the reaction is structure sensitive. If no such effect is found, the reaction is structure insensitive. In both cases, important conclusions can be reached about the mechanism of action of the catalytic material.

Research Report:

In an extensive series of investigations, a series of palladium and platinum catalysts on various supports and with metal particle sizes in the range from 1 to 10 nm were prepared and the surface metal atoms were titrated by reaction of adsorbed oxygen with gas phase hydrogen.

Then turnover numbers for the hydrogenation of cyclohexene in both the gas phase and in the liquid phase using different solvents were measured at various concentrations or partial pressures of cyclohexene and hydrogen. In all cases, the reaction was found to be structure insensitive. This is a striking result, not because this is the first reaction which has been found to be structure insensitive but because of the extent of the work involving two metals, two supports, five solvents and both gas and liquid phase operation.

It is concluded that, in all cases, the working catalytic surface consists of a closely packed two-dimensional metal alkyl compound which does not retain memory of subjacent metal structures. In fact, the working solid catalyst seems to work very much like metal complexes do in solution, as shown for instance in the extensive mechanistic yet unpublished work of Professor Halpern at the University of Chicago.

Reference Publications:

1. R. L. Burwell Jr. and M. Boudart, "Mechanism in Heterogeneous Catalysis," in "Investigation of Rates and Mechanisms of Reactions," E. S. Lewis, Ed., Chapter 12, John Wiley and Sons, New York 1974.

2. M. Boudart, "Surface Science and Catalysis," Chemtech 4, 748 (1974).

3. H. Topsøe, J.A. Dumesic and M. Boudart, "Mössbauer Spectra of Stoichiometric and Nonstoichiometric Fe_3O_4 Microcrystals," J. de Physique 35, C6-411 (1974).

4. M. Boudart, "Chemisorption During Catalytic Reaction on Metal Surfaces," J. Vac. Sci. Technol. Vol. 12, No. 1, 329 (1975).

5. A. Frennet, "Chemisorption and Exchange with Deuterium of Methane on Metals," Cat. Rev.-Sci. Eng. 10(1), 37 (1974).

6. Frank L. Williams and D. Nason, "Binary Alloy Surface Compositions from Bulk Alloy Thermodynamic Data," Surface Sci. 45, 377 (1974).

10. INTRINSIC CHEMICAL REACTIVITY

John I. Brauman, Professor, Chemistry

Graduate Students:

S. R. Aragon	H. L. McPeters
O. I. Asubiojo	L. P. Miller
D. R. Bauer	T. J. O'Leary
C. W. Cornelius	W. N. Olmstead
L. B. Ebert*	K. J. Reed
W. E. Farneth	A. H. Zimmerman
R. Gooden	

*Received Ph.D. during report period.

Agency Support:

NSF GP-37044-X

Technical Objective:

To obtain an understanding and separation of intrinsic (molecular) factors and solvation phenomena which affect chemical reactivity.

Approach:

We study a variety of chemical reactions both ionic and molecular, in both the gas and condensed phase. Comparison of results allows us to understand intrinsic effects (from the gas-phase) and intrinsic plus solvation effects (from condensed phases).

Research Report:

(1) Gas-Phase Ionic Reactions

Graduate Students: O. I. Asubiojo
W. E. Farneth
R. Gooden
W. N. Olmstead
K. J. Reed

We have continued to explore a variety of reactions, studying both equilibria and kinetics by ion cyclotron resonance spectroscopy. We have studied proton transfer from alcohols and thiols. We have developed a technique for examination of neutral products in ion-molecule reactions and used this to study the stereochemistry and products of nucleophilic displacement reactions. We have explored the rates of a number of displacement reactions and slow proton transfers in an effort to determine the underlying physical principles. Because some of these reactions are very slow, we have had to develop new techniques for our data analysis. We have also explored reactions involving displacement at carbonyl carbon and demonstrated the existence of a minimum on the potential surface - a tetrahedral intermediate.

Current work is directed modeling these slow reactions, using RRKM and related theory.

(2) Electron Affinities, Photochemistry of Ions

Graduate Students: H. L. McPeters
K. J. Reed
R. Gooden
A. H. Zimmerman

By studying thresholds for photodetachment of electrons from negative ions, we are able to determine electron affinities for the corresponding neutrals. We have found thresholds for SiH_3^-, GeH_3^-, CF_3^-, SiF_3^-, phenoxide ion, pyrrolate ion, and some alkoxide ions. We have used these data to infer bond dissociation energies in neutrals. A recent development involves understanding the shapes of photodetachment cross sections as a function of energy. This provides information about geometries and electron distribution in ions. A theoretical calculation on isomers of NO_2^- is consistent with our hypothesis that a stable peroxy isomer exists.

(3) Isotope Separation

Graduate Student: T. J. O'Leary

Work done in collaboration with Professor Schawlow (Physics). We have been exploring a variety of methods for isotope separation which make use of some of the unique properties of lasers.

(4) Light Scattering

Graduate Students: S. R. Aragon
D. R. Bauer
C. W. Cornelius
L. P. Miller

Work done in collaboration with Professor Pecora. We have studied molecular reorientation of a variety of molecules. By use of light scattering and ^{13}C NMR we have determined the components of the rotational diffusion tensor for some asymmetric molecules. Our results are consistent with a hydrodynamic model with a slip boundry condition and are in good agreement with calculations using this model. We have also explored motions of polystyrene and find evidence for internal chain motions as well as overall molecular reorientation.

(5) Graphite Intercalates

Graduate Student: L. B. Ebert

Work done in collaboration with Professor Huggins (Material Science). We have explored the structures and chemistry of a number of reaction products of graphite. Some are not intercalates, although reported to be so. Other, new compounds, which are intercalates have been made. We have studied the intercalate of antimony pentafluoride and found liquid-like behavior to unusually low temperatures. We have studied carbon monofluoride and find NMR evidence for a structure containing an infinite array of cyclohexane boats.

Reference Publications:

1. C. A. Lieder and J. I. Brauman, "Detection of Neutral Products in Gas-Phase, Ion-Molecule Reactions," J. Amer. Chem. Soc., 96, 4028 (1974).
2. J. I. Brauman, W. N. Olmstead, and C. A. Lieder, "Gas-Phase Nucleophilic Displacement Reactions," J. Amer. Chem. Soc., 96, 4030 (1974).

3. D. R. Bauer, G. R. Alms, J. I. Brauman, and R. Pecora, "Depolarized Rayleigh Scattering and ^{13}C NMR Studies of Anisotropic Molecular Reorientation of Aromatic Compounds in Solution," J. Chem. Phys., 61, 2255 (1974).

4. P. K. Pearson, H. F. Schaefer III, J. H. Richardson, L. M. Stephenson, and J. I. Brauman, "Three Isomers of the NO_2^- Ion," J. Amer. Chem. Soc., 96, 6778 (1974).

5. D. R. Bauer, J. I. Brauman, and R. Pecora, "Molecular Reorientation in Liquids. Experimental Test of Hydrodynamic Models," J. Amer. Chem. Soc., 96, 6840 (1974).

6. J. I. Brauman, T. J. O'Leary, and A. L. Schawlow, "Isotope Separation by Selective Unimolecular Isomerization," Optics Commun., 12, 223 (1974).

7. L. B. Ebert, R. A. Huggins, and J. I. Brauman, "Wide Line Nuclear Magnetic Resonance of ^{19}F in Graphite-Antimony Pentafluoride: Evidence for Rapid Motion of Intercalated Species," Chem. Commun., 924 (1974).

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11. CRYSTAL CHEMICAL STUDIES OF CRYSTALLINE AND AMORPHOUS SILICATES

Gordon E. Brown, Assistant Professor, Geology

Professional Associate:

P. M. Fenn, Research Associate, Geology

Graduate Students:

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M. P. Taylor

Agency Support:

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Stanford Research Development Fund 2 BBZ-055

Technical Objectives:

(1) to gain a fundamental understanding of the relationships between a mineral's stability and the variables temperature and composition at the atomistic-electronic level. (2) To obtain information concerning the structure and properties of silicate glasses. (3) To study the nature of mineral intergrowths.

Approach:

The crystal structures, compositional variations and electronic energies of naturally-occurring and synthetic crystalline silicates are being investigated by a combination of (1) single-crystal and powder X-ray diffraction methods over a range of temperatures (24°-1100°C); (2) X-ray emission microanalysis; (3) transmission electron microscopy; (4) photoelectron spectroscopy; and (5) semiempirical quantum chemical calculations on representative molecular fragments of silicate structures. Estimates of stability differences between various structural perturbations of silicates are obtained by semiempirical molecular orbital and electrostatic energy calculations. Structural variations in synthetic silicate glasses are being studied by X-ray radial distribution analysis and photoelectron spectroscopy.

Research Report:

(1) High-Temperature X-ray Diffraction Studies of Silicate Structures

Professional Associate: P. M. Fenn

Graduate Students: B. G. Aitken
M. P. Taylor

Structural studies of rock-forming minerals as a function of temperature yield important information about a number of subsolidus features such as structural expansion, phase transformations, exsolution mechanisms and kinetics, intracrystalline cation exchange, domain structure and thermal motion of atoms. Such information is useful to the earth scientist because of its bearing on mineral geothermometry and interpretation of the thermal history of rocks. For this work we are using high-temperature furnaces, mounted on a precession camera and an automated 4-circle diffractometer, which are capable of continuous operation at temperatures up to 1100°C. We have completed a study of the structural changes in synthetic sphene ($CaTiSiO_5$) as a function of temperature. A nonquenchable, reversible $\underline{P2_1/a} \rightleftarrows \underline{A2/a}$ transition was found to occur at 220°C (5,9). The transition mechanism was studied by crystal structure analysis at a series of temperatures up to 750°C. The major change at the phase transition is movement of the Ti atom from an off-centered to centered position in its octahedron. This mechanism is very similar to that observed during the ferroelectric to paraelectric transition in $BaTiO_3$. However, the antiparallel dipole alignment in sphene suggests antiferroelectric behavior.

We have continued our study of a synthetic, compositionally intermediate, hypersolvus alkali feldspar in which evidence for ordering of Na and K within the alkali cavity was found (2). Transmission electron microscopy failed to show evidence for phase separation. These results suggest that the ordering is on a scale of several unit cells. The splitting vector between the Na and K half-atoms is approximately parallel to the commonly observed plane of intergrowth, $(\bar{6}01)$, in unmixed Na-K feldspars. The proposed ordering of Na and K may therefore mark the beginning of subsolidus unmixing. We are currently studying the structural expansion of this phase as a function of temperature up to 1000°C. Comparison of these data with high-temperature data for the

Na and K feldspar end-members should provide further information concerning the unmixing mechanism.

We have recently initiated a high-temperature X-ray study of natural staurolite ($Fe_2Al_9Si_4O_{23}OH$) in which weak violations of space group symmetry Ccmm have been observed, resulting in monoclinic C2/m symmetry. The possibility of a quenchable C2/m→Ccmm transition is being investigated. Such a transition may have bearing on sectoral-compositional zoning in staurolites.

(2) Photoelectron Spectroscopy of Crystalline and Amorphous Silicates

Professional Associate: P. M. Fenn

We are continuing our study of electron binding energies in various crystalline and amorphous silicates in an attempt to detect differences in Al, Si and O coordination environments. A number of crystalline and amorphous silicates have been examined using both Hewlett-Packard and Varian ESCA spectrometers. Our results to date$^{(4)}$ indicate that coordination number differences between Al in various compounds are not detectable. We have observed shifts of up to 2 ev in the core level binding energies of Al, Si, and O between crystals and glasses of alkali feldspar compositions. Much smaller differences have been observed between α-quartz and silica glass. Correlations between oxygen coordination, electronegativities of metal cations and the Si(2S) and O(1S) binding energies in a number of compounds have also been observed.

(3) Semiempirical Molecular Orbital Calculations

Graduate Student: B.H.W.S. de Jong

The importance of cation-cation repulsive forces in determining the minimum potential energy configuration of atoms in minerals has been well known for some years. We have carried out a number of calculations on representative molecular fragments of silicate structures, chosen to simulate different amounts of cation-cation interactions, employing the CNDO/2 formalism with several modifications$^{(3)}$. In particular we have found that the ordering of electronic binding energies for the charged fragments Al_2O_{11}, Al_2O_{10} and Al_2O_9, exhibiting corner-, edge and face-sharing of octahedra, respectively, is correct only if a charged spherical potential about the fragment is added to to the calculation. Our results suggest that the stability differences between these fragments arise in large part from the interaction of the fragment with the surrounding structure. Calculations involving the fragments Si_2O_7, Si_2O_6, Si_2O_5, $SiAlO_7$, $SiAlO_6$, $SiMgO_9$, $SiMgO_8$ and $SiMgO_7$ are now underway.

(4) Electrostatic and Repulsive Energies of Silicates

Professional Associate: P. M. Fenn

As part of our study of the factors affecting a mineral's stability, we have calculated the electrostatic energies of a number of silicates employing Bertaut's electrostatic energy summation procedure. Nearest-neighbor repulsive forces are estimated using bulk modulus data for simple oxides and fluorides. We have concentrated primarily on the potential energy differences among a number of structural models of the intermediate alkali feldspar discussed in research report (1). Our results indicate that the alkali cavity has two distinct potential energy minima, supporting our conclusions concerning Na-K ordering. A calculated energy difference of 12.6 kcal/mole exists between the structural model with the alkali atom occupying the center of its oxygen polyhedron and that with the alkali atom slightly off-center. The minimum energy, off-centered position corresponds to the position determined experimentally.

(5) X-ray Radial Distribution Studies of Synthetic and Natural Silicate Glasses.

Graduate Student: M. P. Taylor

Indirect information concerning the state of aggregation in silicate liquids may be obtained by studies of silicate glasses of various compositions. As part of a general, interdisciplinary study of crystallogenics in magmatic rock-forming systems, we have begun an investigation of structural variations in glasses from the system $NaAlSi_3O_8$ (Ab)-$KAlSi_3O_8$(Or) - SiO_2(Q), utilizing radial distribution techniques. Efforts so far have been devoted to developing data gathering and reduction procedures as well as to the construction of a Mo-wound furnace for glass synthesis. We are using a Picker Facs-I diffractometer operated in the step-scanning mode in steps of $\sin 2\theta/\lambda$

for data collection on small diameter cylinders of solid glass. Radial distribution functions are calculated using the recently developed least-squares procedure of Konnert and Karl (1973, Acta Crystallog. A29, 702). Experiments are now underway on synthetic glasses in the Ab-Or-Q system.

(6) Characterization of Two-Phase Mineral Intergrowths

Graduate Student: K. D. Keefer

Because of the potential information that intergrowths contain concerning the crystallization, subsolidus cooling history and alteration of rocks, we have begun a study of several types of mineral intergrowths including perthitic feldspars from volcanic and hypabyssal igneous rocks and pyroxene-amphibole intergrowths from eclogites. Perthites consist of intergrowths of Na- and K-rich feldspars on scales ranging from submicroscopic (cryptoperthities) to macroscopic (macroperthites). Because the intergrown phases differ in unit cell dimensions, they are commonly strained relative to the pure Na and K end-member feldspars. We are currently studying the relationship between two-phase interface area and degree of strain at the unit cell level. Our primary aim is to gain an understanding of the origin of these intergrowths.

A second area of study involves the origin of unusual intergrowths of amphiboles and pyroxenes of possible mantle origin.

(7) ^{57}Fe Mössbauer Studies of Minerals

Graduate Student: B. M. Taylor, Geology

Consultant: Professor B. B. Triplett, Physics

^{57}Fe Mössbauer spectroscopy has become an important method of determining Fe^{2+}/Fe^{3+} ratios and intracrystalline distributions of Fe in silicate minerals. With the aid of Dr. B. B. Triplett, an ^{57}Fe Mössbauer spectrometer has been assembled. We are currently investigating the site distribution of Fe and the Fe^{2+}/Fe^{3+} ratios in a number of amphiboles from a skarn. One of the purposes of this study is to search for a correlation between the ordering of Fe^{3+} in one of the four octahedral sites and the deuterium content of these amphiboles.

(8) Environmental Asbestos Study at Stanford

Undergraduate Student: David Dinter, Geology

Consultant: A. J. Sidlow, Safety and Health

Because of the potential health hazards of ingestible fibrous minerals and ceiling tile, we have begun a survey of campus buildings to check for the presence of asbestos that can readily become airborne or enter into water supplies. Preliminary results indicate that several sites do show detectable asbestos in dust samples.

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12. PHOTOELECTRONIC PROPERTIES OF SOLIDS

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** Received Engineer's Degree during report period.

Agency Support:

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Technical Objective:

To investigate the photoelectronic properties of solids, both crystalline and non-crystalline, in order to understand the underlying phenomena and to improve the properties and performance of electronically active materials and devices.

Approach:

To couple a materials synthesis program closely to a utilization of a range of electrical conductivity, photoconductivity, luminescence, Hall and photo-Hall effect, thermoelectric and photothermoelectric effect, capacitance and photocapacitance, and optical measurement techniques, in order to investigate the properties of imperfections and structures involved in charge transport under the combined influence of optical excitation, thermal gradients, electrical and magnetic fields, and as a function of material composition.

Research Report:

(1) Applied Research on II-VI Compound Materials for Heterojunction Solar Cells

Graduate students: J. Aranovich
F. Buch
R. Champion
K. Mitchell

p-CdTe/n-CdS and p-CdTe/n-ZnCdS heterojunctions show promise to provide cells for solar energy conversion with maximum theoretical efficiency in the 17-23 percent range. They are representative of several systems of II-VI heterojunctions of interest for this purpose, including also p-ZnTe/n-CdSe, p-ZnTe/n-CdTe and p-CdTe/n-ZnSe. Cells with the presently observed magnitude of reverse saturation current are capable of a maximum efficiency of 10-13 percent. Without optimization of parameters, cells made to date show an efficiency of 3-4 percent. Major research efforts are directed toward the dependence of quantum efficiency, reverse saturation current and contact resistance (particularly to p-CdTe) on preparation variables.

Large grain size in p-CdTe films deposited by the close-spaced vapor transport method on single crystal n-CdS was achieved by varying the temperature-time profile of the source and substrate. With a "cross-over" temperature-time profile, in which the temperature of the source is raised while the temperature of the substrate is lowered, grain sizes of 30 to 60 microns were obtained. The corresponding lateral resistivity of the film was less by a factor of 30 than the resistivity of a film prepared with a "normal" temperature profile in which both source and substrate are brought to temperature simultaneously. This technique may be applicable to a variety of film deposition processes.

The formation of reproducible, stable, low-resistance, ohmic contacts to p-CdTe is essential for desired cell performance. For a minimum loss due to contact resistance, this resistance should not exceed about 0.2 ohm cm^2 for a p-CdTe/n-CdS cell. It has been found that desirable contacts can be made with Ni to 2-4 ohm-cm p-CdTe single crystal material with a contact resistance of 0.15 ohm cm^2 by an etch with $K_2Cr_2O_7:H_2SO_4:H_2O$ followed by a heat treatment. Our understanding of the process involves the formation of a thin Te layer by the etch, followed by diffusion of this layer into the p-CdTe to produce a p^+ layer between the Ni and the bulk CdTe, thus allowing tunneling between the Ni and the narrowed Schottky barrier to the p^+-CdTe. Excessive heating causes a solid-solid reaction and formation of nickel tellurides, which form a non-ohmic Schottky barrier with CdTe. Auger spectroscopy analysis of Ni contacts on etched p-CdTe support this interpretation; an abrupt metal-semiconductor junction is observed before heat treatment and after heat treatment at 275°C, but there is a continuous variation of Cd and Ni across the same region after heat treatment to 450°C.

A large increase in the versatility of our approach to the preparation of thin or thick film cells is provided by our acquisition and development of a vacuum evaporator. After an initial period of use for contact studies, the Knudsen cells of the new evaporator will be charged with S, Cd and Te (or with CdS and CdTe), and the evaporation of CdS and CdTe films will proceed.

We are also investigating ion implantation of the CdTe with P or As to improve contacts and/or give higher film conductivity. We have initiated an investigation of fabrication procedures for In_2O_3/SnO_2 conductive transparent films to be applied to the CdS.

Heterojunctions of p-ZnTe/n-CdSe have been prepared by the close-spaced vapor transport deposition of n-CdSe films on single crystal p-ZnTe. Ohmic contacts were made with Au or Ni to p-ZnTe, following the same etch and heat treatment schedule as for p-CdTe. Three cells have been prepared and values of quantum efficiency of 0.5 are indicated. This system is of interest because it offers the only II-VI opportunity for making a zero lattice-mismatch junction.

(2) Photoelectronic Properties of Amorphous Chalcogenides

Graduate students: J. E. Mahan Chan Jo Park
R. T.-S. Shiah

Photoconductivity analyses have been made for the following three categories of amorphous semiconductors: (1) V-VI materials: As_2Te_3, Sb_2Te_3, As_2Se_3, As_2Se_2Te; (2) IV-V materials: $Sn_{55}As_{45}$, $Ge_{41}Sb_{59}$, $Ge_{57}Sb_{43}$; (3) IV-VI materials, Ge-Te alloys: $Ge_{22}Te_{77}$, $Ge_{36}Te_{64}$, $Ge_{40}Te_{60}$, $Ge_{47}Te_{53}$, $Ge_{50}Te_{50}$, $Ge_{67}Te_{33}$. Measurements include dark conductivity vs temperature, photoconductivity vs light intensity and temperature, thermoelectric power vs temperature, optical transmission, and field effect. If photoconductivity characteristics in which the maximum photoconductivity occurs with a magnitude of about the same as the dark conductivity at that temperature is called Type I, and a photoconductivity much less than the dark conductivity usually without a maximum is called Type II, all V-VI materials show Type I photoconductivity, all IV-V materials show Type II, and IV-VI materials show Type I if the atomic fraction of IV is $\leq$ atomic fraction of VI, and Type II if the atomic fraction of IV is $>$ atomic fraction of VI.

A close examination of the numerical values of energy and kinetic parameters for the family of V-VI materials reveals a close scaling of energy parameters with optical absorption gap. Furthermore it is found that for all four materials $KG_c^2 = 10^{37}$ and $N_{fo}K''G_c = 4 \times 10^{27}$, where K is the pair recombination coefficient between localized states near the mobility edges, G_c is the density of localized states near the conduction edge, N_{fo} is the density of localized states at the equilibrium Fermi level, and K'' is the pair recombination coefficient between localized states near the valence edge and localized states near the equilibrium Fermi level.

The observed differences between Type I and Type II photoconductivity behavior as described above can be interpreted in terms of the absence of dominant pair recombination between localized states near the mobility edges in Type II materials, because of a much smaller density of such localized states at the minority mobility edge.

Annealing at 100°-200°C (below the crystallization temperature) for 10 min has negligible effect on the behavior of V-VI and IV-V materials, but strongly affects Ge-Te alloys. Upon annealing, the magnitudes of the dark conductivity and photoconductivity decrease, and the dark conductivity activation energy increases. The photoconductivity behavior of $Ge_{50}Te_{50}$ changes from Type I to Type II upon annealing. Crystallization of several V-VI and IV-VI materials increases the dark conductivity by a factor of 10^7 - 10^9, and the photoconductivity by a factor of 10^3 - 10^6 at 150°K.

Field effect measurements have been made on As_2Te_3, As_2SeTe_2, Ge_2Te_7, GeAs and $GeAs_2$. Changes in conductance upon application of a field voltage can be interpreted as being the result primarily of capture of charge by localized states or by change in the "free" carrier density. Although we had expected the first process to be dominant, we have been surprised to find a number of evidences rather strongly favoring the "free" carrier interpretation of the field effect. Over the measured range, the field effect in GeAs and $GeAs_2$ appears to be clearly describable in terms of localized state effects in a two-carrier conductivity situation; in As_2SeTe_2 the effect appears to be wholly a "free" carrier effect; and in As_2Te_3 the effect appears to be controlled by "free" carriers at higher temperatures and by localized states at lower temperatures.

As_2SeTe_2 provides the best evidence for a "free" carrier interpretation. The calculated densities vary rapidly with temperature over the entire range of temperature available for the measurement. Further, the measured field effect plots (change in conductance vs field voltage) do not show enough curvature in the accumulation region to be matched well by theoretical localized state field effect curves. The data, however, can be matched well by a theoretical "free" carrier field effect curve with a "free" hole density of 1.2×10^{17} cm^{-3}, an equilibrium Fermi level kT below the middle of the gap, and an electron to hole mobility ratio of 0.03 (at 295°K). From the measured conductivity at this temperature, the majority carrier (hole) mobility is calculated to be 10^{-5} cm^2/V-sec.

As_2Te_3 shows a rapid variation with temperature of the calculated densities above 0°C, but a small temperature variation below 0°C. This observations suggests that below 0°C the field effect is controlled by localized states at the Fermi level, and that above 0°C the field effect is controlled by "free" carriers. At 0°C, where these two densities are equal, the localized state density is about 10^{19} cm^{-3} eV^{-1} and the "free" carrier density is about 2.4×10^{17} cm^{-3}.

If the "free" carrier interpretation is correct, we have through the field effect an independent method of determining this carrier density, which should be extremely useful in interpreting other transport data.

(3) Photothermoelectric Effects in Semiconductors

Graduate students: Y. Ma H. A. Vander Plas
J. McKenzie

Striking two-carrier thermoelectric power effects are found in measurements with amorphous Ge_xSb_y materials. At high temperatures n-type conductivity in extended states is indicated, and at low temperatures p-type conductivity in localized states. $Sn_{55}As_{45}$ is p-type at all temperatures, but indicates extended state conductivity at high temperatures and localized state conductivity at low temperatures.

Thermoelectric power measurements on Ge_xTe_{1-x} alloys indicate p-type conductivity for $x \leq 0.50$, over the whole range of temperature and with a linear thermoelectric power vs 1/T plot. For the Ge-rich sample, $x = 0.67$, the thermoelectric power is negative with an activation energy of 0.09 eV in the high temperature range, but for $T < 285°K$ the thermoelectric power becomes constant. This observed transition from positive to negative thermoelectric power with increasing Ge/Te ratio supports the hypothesis that 2-carrier conductivity effects dominate Ge-Te alloys.

If it is desired to harmonize the field effect "free" carrier densities mentioned above with the densities determined from thermoelectric power measurements on the same V-VI amorphous materials, it is necessary to use an "effective density of states" parameter in the reduction of the thermoelectric power data that is several orders of magnitude larger than that commonly found in semiconductors. Such a result may be consistent with a high density of states at the mobility edge.

Considerable effort has been devoted to developing reliable methods to prepare CdS films by the solution-spraying method, in which a solution of $CdCl_2$ and thiourea is sprayed onto a heated substrate. It is our purpose to determine the effects of film structure on transport properties, and in turn the effects of preparation procedures on film structure. This investigation is also of interest because the solution-spraying method appears to be by far the most economical way to deposit thin-film CdS for either the p-Cu_2S/n-CdS or p-CdTe/n-CdS thin film solar cells. The parameters that affect the properties of the film in preparation are the substrate temperature, the volume spray rate, and the cooling rate of the substrate after spraying. A broad series of thermoelectric and photothermoelectric measurements are planned to characterize these films electrically and photoelectronically. The solution-sprayed CdS films obtained in our work represent some of the most conducting films prepared by this process to date. Films deposited at 500°C have a dark electron density of 4×10^{16} cm^{-3} independent of T, and a dark electron mobility of 6 cm^2/V-sec at 300°K (10 cm^2/V-sec in light). Solution-sprayed films of CdS with a room temperature conductivity of 0.1 $ohm\text{-}cm^{-1}$ should be possible and of considerable interest for solar cells utilizing thin-film CdS.

An investigation of transport in sublimed films of $Ir(CO)_{2.93}Cl_{1.07}$ has also been continued. Over some 30 films there appears to be a fairly good correlation between the magnitude of the conductivity activation energy (from 0.052 to 0.239 eV) and the magnitude of the thermoelectric power (from 4 to 660 microV, respectively). Samples with both high and low values of thermoelectric power appear to have only a slight temperature dependence of this power.

(4) Investigation of Deep Impurity Levels in GaAs by Photocapacitance and Related Techniques

Graduate students: S.-H. Chiao and P. Vasudev

The work on this project can be conveniently summarized under four categories: (1) photocapacitance measurements on LPE GaAs on high-resistivity GaAs substrates using Schottky barriers, and on LPE GaAs on p^+ GaAs substrates using the junction formed in this way; (2) evaluation of the significance of the "excess capacitance," C_o required to linearize a $1/C^2$ vs V plot; (3) growth of LPE GaAs with controlled properties and good surface morphology; and (4) evaluation of LPE GaAs containing Cu (and eventually other) impurities.

Observed curvatures in measured $1/C^2$ vs V plots can frequently be removed or decreased by plotting instead $1/(C-C_o)^2$ vs. V, where C_o is obtained as the intercept of a C vs $V^{-1/2}$ plot. These linearized plots also show good agreement between indicated carrier densities and values obtained independently from Van der Pauw data. It is believed that the "excess capacitance" C_o may be a useful parameter in describing departures of the junction from ideal behavior. Measurements of C_o show the following: (a) C_o does not depend on the electrode geometry, (b) the value of C_o is fairly constant across a given layer, (c) C_o increases with increasing carrier density (from about 7 pf at 2×10^{14} cm^{-3} to 20 pf at 10^{15} cm^{-3}), (d) C_o decreases with increasing breakdown voltage (from about 40 pf for V_B = 4 V to about 5 pf at V_B = 56 V), and (e) C_o has a frequency dependence that varies with both the reverse bias used and with the temperature. The dependence of C_o on V_B is much larger for material with a higher carrier density. It seems likely that C_o is connected with material inhomogeneity and deep level traps at the metal-semiconductor junction or within the layer. It was also determined that C_o is larger for bulk material than for an LPE layer with the same carrier density, and that C_o increases with time after the application of voltage in a capacitance measurement (by about 30 pf in three cells with initial C_o values of 5, 11 and 38 pf).

Schottky barrier photocapacitance measurements were made with Au electrodes on several LPE GaAs layers. At 300°K no persistent photocapacitance was observed, but at 90° to 100°K photocapacitance effects were observed for intrinsic photoexcitation, and for extrinsic photoexcitation corresponding to excitation energies of 1.07 and 0.83

eV. Estimates of trap density gave values of about 1.5 x 10^{15} cm^{-3} and 1.4 x 10^{14} cm^{-3} respectively. The total average trap density calculated from the intrinsic photoexcitation was 5.3 x 10^{15} cm^{-3}.

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13. ATOMIC MERCURY ANTI-STOKES FREQUENCY CONVERSION

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Agency Support

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ERDA E(29-2)3570
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DAHC 04-74-C-0033

Technical Objective

To design and construct apparatus in order to experimentally demonstrate anti-Stokes frequency up-conversion in atomic mercury vapor.

Approach

A proposed frequency up-conversion in atomic mercury is based on the electronic anti-Stokes Raman transitions from the singlet 6^1P_1 to the triplet $6^3P_{0,1,2}$ states. The operational requirements are a population inversion in the singlet state with respect to the triplet states and an intense input laser radiation to generate anti-Stokes Raman scattering from the singlet state. With an input laser wavelength of 1.06 μm, up-conversion to 5148 Å and 4157 Å are expected.

One method of experimental demonstration being considered involves optical pumping with a tunable laser. A significant population in the singlet $^1P_1$ state is to be obtained by first exciting the ground state atoms to the 7^1S_0 state via two-photon absorption of 3128 Å output of a tunable source (e.g. second harmonic generation with a dye laser). The 7^1S_0 state rapidly decays to the singlet $^1P_1$ state whose radiative lifetime is effectively increased due to radiation trapping.

The relatively long-lived $^1P_1$ state leads to the required population inversion. A cell containing the inverted atomic mercury vapor is then irradiated with an intense beam of 1.06 μm radiation from a Nd:YAG laser in order to generate anti-Stokes Raman scattering from the singlet state at 5148 Å and 4157 Å. Because of the population inversion both 5148 Å and 4157 Å stimulated transitions are amplified while the input radiation is attenuated. The amplification of the anti-Stokes Raman transition therefore results in the frequency up-conversion of the input wavelength.

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14. STUDIES IN HOMOGENEOUS CATALYSIS AND THE SYNTHESIS OF METAL-METAL BONDS

James P. Collman, Professor of Chemistry

Professional Associates:

- S. E. Hayes
- H. Ledon
- J. L. Roustan
- G. Schmuckler
- R. Wahren

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- D. H. Davis*
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- R. R. Gagne*
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- M. L. Marrocco
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Agency Support:

NSF MPS70-01722-A03
ARPA through CMR, DAH C15-73-G15
NIH GM17880
NATO 504
NSF GP39451

*Received Ph.D. during report period.

Technical Objectives:

This research has two goals--(a) to synthesize soluble, linear conductors in order to examine the excitonic theory for high-temperature superconductivity; and (b) to develop new homogeneous and heterogeneous catalysts.

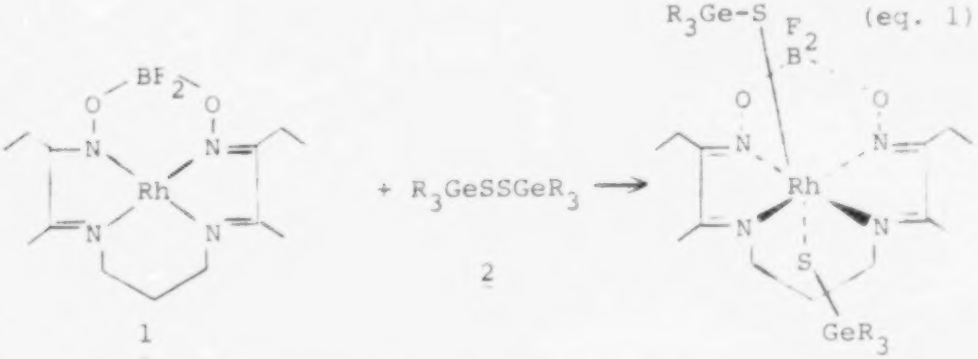
Approach:

We have five major research efforts: the synthesis of linear molecular polymers with backbones comprised entirely of metal-metal bonds, the preparation of iron(II) porphyrin complexes which can serve as models for the mixed-function oxygenase enzymes, the characterization of hybrid homogeneous-heterogeneous catalysts, the preparation of catalytic electrodes, and the development of metallic reagents for practical organic synthesis.

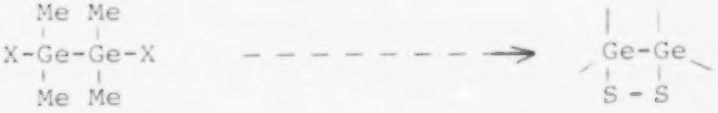
(1) The Synthesis of One-Dimensional Intermetallic Polymers

We have been working on synthetic methodologies directed towards the ultimate preparation of unidimensional intermetallic polymers. Our interest in such materials stems from the expectation that a coaxially oriented solid derived from such substances might exhibit anisotropic electron transport properties which would be principally dependent upon the structure of the individual polymer molecules. This work is being carried out as part of a long standing collaborative effort with Professor W. A. Little, Physics, in a program directed towards examining the feasibility of Little's hypothetical excitonic superconductor.

During the past year we have developed a new reaction which might be used to prepare a polymer having in its backbone the repeating unit: -Ge-Ge-S-Rh-S-. The key reaction is the addition of germanium disulfides 2 to neutral rhodium macrocycles 1 (eq. 1). Work in progress is directed towards a general synthesis of cyclic germanium disulfides 3 (and diselenides) (eq. 2).



1 2 (eq. 1)



3 (eq. 2)

(2) Models for Mixed-Function Oxygenases

During the past year we have prepared and characterized iron porphyrins having mercaptide anions as axial bases, reproducing the unusual esr and electronic spectra characteristic for three of the four recognized stages of cytochrome P_{450}. These studies have clarified the coordination sphere in this widespread and extremely important class of hydroxylating enzymes. Further syntheses, full characterization of these iron porphyrins by Mossbauer, vibrational spectra, and X-ray diffraction are in progress.

(3) Catalysts Bound to Solid-State Supports

Work in this area continues in collaboration with Professor Michel Boudart, Department of Chemical Engineering. We have chemically attached a series of transition metal complexes to the surface of spherical, porous silica particles having very large surface areas ($350\ m^2\ g^{-1}$). During the past year we have been attempting to prepare new silated ligands for these catalytic studies. So far this work has not come to fruition. We have turned some attention to polymeric organic ligands.

(4) The Preparation of Catalytic Electrodes

This new project is partially derived from our studies of oxygen binding iron porphyrins and catalysts bound to solid-state supports. We are attempting to prepare "face to face" binary porphyrin complexes which should rapidly reduce molecular oxygen in the inter-porphyrin cavity. We plan to attach members of this new class of porphyrins to conducting surfaces affording catalytic oxygen cathodes for ultimate use in fuel cells. This project is part of a large joint effort involving Boudart (Chem. Engineering), Taube (Chemistry), Anson (Chemistry, California Institute of Technology) and Tennent (Hercules Corp.). Our efforts in progress concern porphyrin synthesis and electrochemical characterization of $NbSe_2$ and TaS_2.

(5) Iron Carbonyl Reagents for Organic Synthesis

We have continued our exploration of iron tetracarbonyl dianion as a reagent for organic synthesis. This remarkable compound carries out many of the same reactions effected by the Grignard reagent, but the iron compound reacts with stereoselectivity and also tolerates a wide range of organic functional groups. During the past year we have nearly completed our studies of reaction mechanisms and the unusual role of ion-pairing in these systems. The mechanisms by which $Na_2Fe_2(CO)_8$ selectively reduces activated olefins has been greatly clarified. These studies have been carried out in collaboration with Brauman (Chemistry). A review of our efforts in this field has been accepted for publication and several manuscripts are in advanced stages of preparation. Our work in this area should be completed in another year.

Publications:

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15. INTERACTIONS OF SOLIDS WITH SOLUTIONS

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**Received MSc during report period.

Technical Objectives

The interaction of aqueous solutions with rocks and minerals is being studied at temperatures from 25 to 500°C and 1 to 2000 bars by use of gold-cell hydrothermal solution equipment. The equilibrium and kinetic behaviour of chemical systems relevant to understanding geochemical processes is determined. Some studies of metallic sulfide equilibria and sulfur isotopes are being done to clarify subsidiary questions.

Research Report:

Phase relations in the system Tl_2S-As_2S_3 from 200 to 450°C were determined. Phases encountered, in addition to liquid, were carlinite (Tl_2S), lorandite ($TlAsS_2$), orpiment (As_2S_3), and a previously unknown crystalline compound, Tl_3AsS_3. The work is being written up as part of the MSci Thesis of J. A. Peterson. The reaction of pyrite (FeS_2), pyrrhotite (FeS), quartz (SiO_2), and gold (Au) with $NaCl$-H_2O solutions was done from 100°-500°C, 500-1500 bars, and up to 10 wt.% NaCl. The work was presented at an international scientific meeting and a portion has been submitted for publication. It will serve as the experimental part of the PhD dissertation of J. J. Rytuba, now being finished. A major effort published this year was a study of the reaction of basalt with sea water at 200°C and 500 bars, done jointly with Dr. Bischoff of the U. S. Geological Survey. Further studies are now going on, with the support of a grant from the National Science Foundation. The reaction of granite with dilute aqueous solution is being done as part of the lithium project of the U. S. G. S., which is directed by Dr. Vine. The work is being done in liason with the Geothermal Energy project in the Schools of Earth Science and of Engineering, Stanford. Studies of the interaction of petroleum with water as a function of temperature and pressure are being done in liason with Dr. Price of the U. S. G. S., and the interaction of hydrocarbon-containing rocks with water are planned. The distribution of sulfur 34 between sulfate and sulfide sulfur in aqueous solutions is being studied at 500°C and 1500 bars.

Reference Publications:

1. Rytuba, James J. and Dickson, Frank W., 1974, Reaction of pyrite + pyrrhotite + quartz + gold with $NaCl-H_2O$ solutions, 300-500°C, 500-1500 bars, and genetic implications, 4th Symposium, Int. Assoc. Ore Genesis, Varna, Bulgaria (Abstract).

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16. METHODS OF QUANTUM FIELD THEORY APPLIED TO MATERIALS PROBLEMS

S. Doniach, Professor, Applied Physics

Professional Associates:

B. A. Huberman[+]
R. A. Klemm
G. F. Mazenko
J. Zittartz

Graduate Students:

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D. M. Lublin
D. K. Misemer**
E. H. Rezayi
L. A. Turkevich

*Received PhD during report period
**Received MS during report period

Agency Support:

Army AROD DAHC04-74-G-0222
NSF through CMR

Technical Objective:

To apply the methods of quantum field theory to understanding cooperative phenomena in materials and at surface-to-volume interfaces.

Research Report:

(1) Theory of Photoabsorption Spectroscopy in the X-Ray Region

The basic theory set up by Ashley and Doniach has been applied in quantitative detail by Kincaid to the simple diatomic molecule Br_2. An extensive computer calculation of electron-atom scattering from self consistent atomic potentials has shown a very reasonable ab initio agreement with experiment. We have learned that important inelastic effects occur, however, which cannot be predicted within the one electron theory. This work has been published in Phys. Rev. Letters.

Work by E. Rezayi on the general theory has resulted in an equation incorporating the phase shift for an outgoing electron leaving a core state of a central atom with the theory of multiple scattering of the

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electrons on the neighboring atoms. A group theoretical analysis of this equation should allow the simplification of the multiple scattering problem for simple molecules such as $GeC\ell_4$. Experiments by Kincaid and Eisenberger suggest that there is some kind of "electron trapping phenomenon," or resonant state, near threshold in a caged-in molecule of this type.

(2) Theory of Coupled One-Dimensional Chains

Work by R. Klemm (IBM Fellow) and Hanoch Gutfreund has allowed a calculation of the nature of the superconducting or charged density wave instabilities in coupled one dimensional chains in which the electrons are strongly correlated within each chain. They show that superconductivity is possible under conditions of strong correlation for quasi one-dimensional systems given suitable relationships between the electron-electron coupling parameters.

Work with L. Turkevich has been focussing on a system of coupled one-dimensional chains in which random coupling is allowed to take place between the chains. This is done within a Ginzberg-Landau frame work and simulates the behavior of systems such as KCP studied by Professor Little and collaborators.

(3) Real Space Renormalization Group Theory of Two and Three-Dimensional Systems

The real space renormalization group approach of Nijmeier and Van Leeuwen has been applied by D. Lublin to the two-dimensional x-y model. The results give approximate critical indices for this system, previously only obtainable by the series expansion methods. The work has been published in Physical Review Letters.

Work by J. Fields and M. Vogel in the three dimensional Ising model has been completed using a spin-one renormalization group approach. This is the first time three dimensional Ising critical indices could be calculated without the use of high temperature series methods. This work has been submitted for publication.

(4) Theory of Electron Induced Desorption from Solid Surfaces

Work with D. Misemer has been started on a study of many body effects during an electron stimulated desorption of ions from surfaces. It is known that the desorption rates are very sensitive to the exchange of energy between the ion and the surface. We are studying this using a simple collective electron gas model for solids. An experiment to test these ideas has been suggested and is being planned in collaboration with Ingolf Lindau.

(5) Theory of Dynamic Scaling in Ferromagnets

An extension of renormalization group techniques to incorporate hydrodynamic sum rules has been applied to the theory of critical fluctuations in a ferromagnet by G. Mazenko and S. Ma. This has appeared in Physical Review Letters. A longer account is being written up.

Publications

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6. B. M. Kincaid and P. Eisenberger, Phys. Rev. Letts. (June 1975).
7. G. F. Mazenko and S. Ma, Phys. Rev. Letts. (1975).

17. EXPERIMENTS AT LIQUID HELIUM TEMPERATURES ON MACROSCOPIC QUANTUM EFFECTS, MATERIAL PROPERTIES, GENERAL RELATIVITY, AND SUPERCONDUCTING ACCELERATORS

W. M. Fairbank, Professor of Physics
C. W. F. Everitt, Adjunct Professor
R. P. Giffard, Assistant Professor of Physics
H. A. Schwettman, Professor of Physics

Professional Associates:

- J. T. Anderson
- I. Ben Zvi
- D. P. Boyd
- B. Cabrera
- P. H. Ceperley
- L. Elias
- P. Kneisel
- L. Knight
- G. C. Li
- J. A. Lipa
- C. M. Lyneis
- J. M. Madey
- J. Malmivuo
- M. S. McAshan
- H. J. Paik
- T. Smith
- J. P. Turneaure
- F. van Kann
- F. C. Witteborn

Graduate Students:

- S. P. Boughn
- B. Cabrera*
- D. E. Claridge
- G. S. LaRue
- J. M. Lockhart
- C. M. Lyneis*
- P. L. Marston
- B. J. Neuhauser
- H. J. Paik*
- J. S. Philo
- R. H. Roy, III
- S. R. Stein*
- M. A. Taber
- A. M. Vetter, Jr.
- C. A. Waters
- J. P. Wikswo, Jr.
- E. G. Wilson
- P. W. Worden, Jr.

*Received Ph.D. during Report Period

Agency Support:

AFOSR F44620-73-C-0017 and AFOSR F44620-75-C-0070
AFOSR F44620-70-C-0021 and AFOSR F44620-75-C-0022
NASA NGR-05-020-019
ONR N00014-67-A-0112-0076
NSF GP 38610 and NSF MPS73-08748-A02
NSF GP 38906 and NSF MPS73-08836-A02
NSF GH 39028 and NSF DMR75-15628
NSF GP 39029 and NSF MPS73-08870-A03
NSF GI 34778 and NSF APR72-03447-A03
NSF through CMR

Technical Objective:

This research is directed toward the study of the basic problems of physics using low temperature techniques. In addition to experiments studying the special properties of superconductors and helium for their sake, we exploit their unique properties to perform experiments in other fields of physics such as gravitation and relativity, biophysics and medicine, particle accelerators and the search for fractionally charged particles.

Research Report:

(1) Positron Source

Research Physicist: J. M. Madey

A source of magnetic ground state positrons at energies below 10^{-7}eV is required for operation of the positron free fall experiment. Positrons in this energy range cannot be obtained from natural β+ emitters.

The approach we have adopted is to capture a small number of relatively low energy (100 eV) positrons and to trap them within a solenoidal magnetic field between electrostatic mirrors. Provided that the trap proves to be stable, the positrons can readily be thermalized to energies of the order of 10^{-4}eV. Adiabatic expansion can be used to lower the energy to the required 10^{-7}eV.

(2) Photon Counting Detector

Research Physicist: J. M. Madey

We are developing a photo-electric effect detector for use at millimeter wavelengths. The detector is based on excitation of the $n = 1$ cyclotron level of magnetic ground state electrons trapped in a high Q cavity resonant at the cyclotron frequency. Theoretical estimates of the performance predict a noise temperature less than 1°K and quantum efficiencies of the order of 10%. Such a detector would have immediate application in millimeter wave radio astronomy.

(3) The Anomalous Magnetic Moment of the Free Electron

Visiting Scholar: L. Knight

This experiment is an attempt to make a direct measurement of the magnetic moment of a free electron (g-2). This measurement, if made accurately enough, would be a significant test of quantum electrodynamics since g-2 can be calculated by theory as a power series in the fine structure constant. The direct measurement is made possible by the use of low temperatures to provide a homogeneous magnetic field and an otherwise field-free environment for low energy electrons.

(4) Force of Gravity on Elementary Charged Particles

Graduate Student: J. M. Lockhart
Visiting Scholar: F. C. Witteborn

Low energy electron beam techniques have been developed which permit the measurement of the force of gravity on single electrons and positrons, thus allowing a direct test of the gravitational equivalence of matter and anti-matter. The electron experiment has already been performed, yielding results which seem clear, but which also seem to indicate the presence of an unexplained shielding effect in the metallic drift tubes used in the experiment. Recent work has been directed toward exploring the nature of this shielding effect and the conditions under which it exists. There appears to be strong evidence for the presence of a large temperature dependence in the magnitude of the shielding. Experiments are now in progress to determine the detailed behavior of this temperature dependence. Measurements on the positron await the completion of a source of ultra-low energy positrons; a prototype of this source should be ready for tests in the next few months.

(5) Free Electron Laser

Research Physicist: J. M. Madey
Research Associates: L. Elias
T. Smith

Theory indicates the possibility of amplification due to stimulated emission of magnetic bremsstrahlung (synchroton radiation) in a spatially periodic magnetic field. Useful gain is available from the infrared to the vacuum ultraviolet with the capability for high peak power operation.

Experiments are presently underway in the Hansen High Energy Lab to verify the gain equation and to explore saturation characteristics.

(6) Magnetic Susceptibility of Biological Macromolecules

Graduate Student: J. S. Philo

We have developed a new type of magnetic susceptibility apparatus using a superconducting magnet and a Josephson junction magnetometer. At present we have achieved a sensitivity approaching 10^{-6} of the diamagnetic susceptibility of water. This high sensitivity should allow us to measure the small changes in molecular diamagnetism which occur during such processes as the unwinding of DNA helices, conformation changes in proteins, phase changes in membranes, etc. In addition to high sensitivity, the instrument has a response time of a millisecond, which will allow us to study the kinetics of hemoglobin reacting with carbon monoxide and other fast reactions in solutions.

(7) Development of a Sensitive Cryogenic Gravitational Wave Detector

Graduate Student: S. P. Boughn
Postdoctoral Fellow: H. J. Paik

We have designed and constructed a 1400 pound cryogenic gravitational wave detector. The antenna, which is a cylindrical aluminum bar, is covered with niobium-titanium and has been levitated on a 2 kilogauss magnetic field. The source of this field is a set of five, single layer, "pancake-type" coils which are strung in series and operated in a persistent mode. This levitation scheme provides both uniform support for the detector and acoustic isolation for the detecting system. To sense vibrations in the antenna we are developing a superconducting tunable-diaphragm transducer for the low temperature gravitational wave detector. The transducer consists of a thin circular niobium diaphragm clamped around the edge. Two niobium-titanium pancake coils are located close to the two surfaces of the diaphragm and a third coil coupled to a SQUID is connected in parallel with the two pancake coils. A large dc current is stored in the superconducting loop formed by the pancake coils. When this transducer is attached to the end of the gravitational wave antenna and tuned by means of the dc current to the resonant frequency of the antenna under observation, the diaphragm picks up the motion of the bar, amplifies it by the square root of the mass ratio and converts it into electromagnetic signals in the coils by means of inductance modulation. The ac magnetic field generated in the third coil is detected by an extremely low noise superconducting magnetometer When operating, this detector will be the first instrument sensitive enough to detect predicted gravitational radiation of known astrophysical events in our galaxy. We expect eventually to achieve 10^6 improvement in energy sensitivity over Weber's for our 3m°K gravitational wave detector.

(8) Optical Measurement of Surface Profile of Rotating Liquid Helium

Graduate Student: P. L. Marston

We are examining the surface contour of He II in a rotating "bucket" to attempt to observe the vortex array and other superfluid effects. Coherent optical techniques are employed including the observation of the diffraction pattern, phase contrast image, and Fizeau fringes for light reflected by the fluid surface. The Fizeau interferometry technique has been successfully used to measure the surface profiles of rotating He I and He II. Surface depressions like those predicted for a multiply quantized superfluid vortex were observed for the first time.

(9) Superfluid Helium Flow Through an Orifice Near Critical Velocity

Graduate Student: C. A. Waters

This experiment is designed to observe the small energy and momentum associated with the production of a single vortex ring in superfluid helium. To observe the momentum, a superconducting niobium cavity containing a pressure detecting diaphragm in one wall has been built. The motion of the diaphragm is detected as a change in the resonant frequency of the cavity. Vortex rings will be reated by forcing liquid helium to flow through an orifice above the critical velocity.

(10) Properties of Superfluid Helium-3

Graduate Student: B. J. Neuhauser
Research Physicist: J. A. Lipa

The light isotope of helium, of atomic mass 3, has recently been shown to be a superfluid below a temperature of 2.5 millikelvins. Since the helium-3 atoms are Fermions, the understanding of the condensed state parallels the BCS treatment of superconductivity, but significant generalizations are required. Since the nuclei have a magnetic moment, the state displays interesting magnetic properties which can be probed using NMR techniques and SQUID magnetometry. In addition, the classical superfluid properties manifested in helium-4 are expected. We plan to measure some of these properties, in particular, NMR and second sound, in order to obtain a better understanding of the new state. In order to reach the ultra-low temperatures required, a first class helium-3/helium-4 dilution refrigerator is required, plus an extra stage of cooling using either adiabatic demagnetization of a paramagnetic salt, compressional cooling of helium-3 along its melting curve, or demagnetization of a nuclear spin system.

(11) Experiments in Very Low Magnetic Fields

Postdoctoral Fellow: B. Cabrera

We have obtained magnetic fields smaller than 10^{-8} gauss in a cylindrical superconducting lead shield that is four inches in diameter and thirty inches long. This magnetic field level, an order of magnitude smaller than we had previously obtained, corresponds to at most a few flux quanta trapped in the superconducting shield. We are using a superconducting double point-contact magnetometer with a resolution of 10^{-9} gauss to measure the very small magnetic fields. We have constructed an apparatus to measure the magnetic flux trapped in a superconducting cylinder 1/2 inch in diameter by 4 inches long. We have the sensitivity to see individual flux quanta penetrating the walls of this cylinder, and thus study the pinning of flux in superconductors. One of these shields has been used in conjunction with a detection coil coupled to a SQUID as a magnetic monopole detector. Our present sensitivity is 1/50 of a Dirac monopole. Our data to date is consistent with zero magnetic charge.

(12) Nuclear Polarization of He^3

Graduate Student: M. A. Taber

We have used He^3 optical pumping techniques to produce dilute polarized He^3 and He^4 gas mixtures. Such mixtures have been successfully condensed into a low magnetic field region and the precession of the He^3 magnetization has been observed in an applied transverse field of 10^{-4} gauss by use of a SQUID magnetometer. Initial magnetization has been greater than 10^{-6} gauss with a signal to noise of 1000 to 1. With the He^3 concentration being approximately 10^{-3} this represents a polarization of about 1%. We are presently working on experiments to measure the intrinsic He^3 relaxation time as a function of concentration. This experiment is a continuation of effort devoted to development of a He^3 nuclear gyroscope.

(13) Magnetocardiology (Joint Project with Stanford Hospital)

Graduate Students: R. H. Roy, III
J. P. Wikswo, Jr.

We are developing two new magnetic techniques for non-invasive clinical observation of human cardiac function. The first measures magnetic susceptibility changes associated with the motion of blood within the heart. The second technique involves the use of a superconducting gradient magnetometer to measure the magnetocardiogram, the magnetic field generated by the electrical activity of the heart. We have built a large magnetic shield and a computer signal-processing system. The clinical value of the magnetic field measurements will be determined by studying normal patients and patients with various cardiac diseases.

(14) Search for a Quark

Graduate Student: George LaRue

The purpose of this experiment is to search for fractionally charged particles (quarks) on superconducting niobium spheres supported by a magnetic field. The experiment measures the net electric charge on a niobium ball of mass approximately 5×10^{-5} gm. Fractionally charged particles, if they are contained on a niobium ball, would be observable as a non-integral net charge on the ball. Measurements have been made on four niobium balls with a sensitivity of approximately ±0.02 e, where e is the electron charge. Forces simulating non-integral residual charges have been observed on these balls. The central issue in this experiment is to determine unambiguously whether or not these forces are due to fractional charges or are caused by spurious dipole sources. The apparatus has been rebuilt to increase the speed with which data can be assimilated and processed and to facilitate the identification of spurious dipole effects.

(15) Magnetic Field Penetration into Superconducting Tin Film Cylinders

Graduate Student: E. G. Wilson

A number of Sn cylinders, with wall thicknesses ranging from 5,000 Å to 10,000 Å, have been prepared by vacuum deposition onto quartz substrates. The interior penetration resulting from an axial external field is measured with a 30 MHz SQUID magnetometer as a function of temperature. (The external field is returned to zero before each change in temperature.) Three films have been produced which show nonlocal behavior, in that they are better fit by the nonlocal Pippard (or BCS) theory than by the London "local limit" theory. Other films fall into the local limit regime, due to the shortening of the mean free path produced by the film deposition process. The very small reversed interior magnetic field predicted by the theory for sufficiently nonlocal films (in an approximate temperature and film thickness regime) has not been seen. This is probably because 1) all of the films are more "local" than bulk Sn, and this reduces the predicted reversed field size to an even smaller value; 2) pinholes, present to some extent in all of the films, produce a spurious positive signal.

(16) Microwave Josephson Effect Magnetometer

Graduate Student: D. E. Claridge

We have measured the 9 GHz small signal impedance of a dc biased superconducting niobium point contact. The impedance of the point, measured as a function of the dc bias current shows qualitative agreement with the predictions of the resistively shunted junction model. The dependence of the impedance on the microwave signal level also follows the theory. The system has been improved and measurements are now in progress which should yield data suitable for quantitative comparison with theory. We will also attempt to measure the coefficient of the $\cos\phi$ term in the quasiparticle conductance through its influence on the microwave impedance.

(17) Equivalence Principle Accelerometer

Graduate Student: P. W. Worden, Jr.
Adjunct Professor: C. W. F. Everitt

The experiment is intended to test the application of cryogenic technology to a measurement of the uniqueness of free fall, particularly with regard to investigating the ultimate limitations to sensitivity and a possible earth-orbiting equivalence principle experiment. A pair of superconducting test masses of different materials are suspended in essentially frictionless linear magnetic bearings. The masses are cylindrical with dimensions optimized to minimize gravity gradient effects, and are free to move along the cylinder axis. An electronic control mechanism keeps each mass centered with respect to the casing by tilting the support plane provided by the magnetic bearing. The control efforts required to keep the masses centered are appropriately scaled and subtracted to one part in 10^5, providing a signal proportional to any differential acceleration which may exist. The difference signal may then be recorded and Fourier analyzed to determine the relative amplitudes of the various frequency components.

The limiting sensitivity of the experiment on earth is set by seismic noise and the accuracy of the subtraction process. A difference of one part in 10^{12} in the ratio of inertial to gravitational mass is estimated to be the limit of sensitivity on earth. In low earth orbit the sensitivity is limited by tidal sloshing of the liquid helium refrigerant and is probably one part in 10^{17}.

(18) Relativity Gyroscope Experiment

Adjunct Professor:	C. W. F. Everitt
Research Physicists:	J. T. Anderson J. A. Lipa
Postdoctoral Fellow:	B. Cabrera
Visiting Postdoctoral Fellow:	F. van Kann

In 1960 Professor Leonard Schiff of Stanford University suggested a new test of general relativity based on observing the precessions of very accurate gyroscopes in an earth-orbiting satellite. Since 1962 a group of physicists and engineers from the Hansen Laboratories and the Department of Aeronautics and Astronautics have been designing and developing the experiment using cryogenic techniques. A model of the flight gyroscope and liquid helium dewar has now been operating at Stanford for nearly three years. A low temperature run is in progress in Room 002 of the Physics basement.

(19) Superconducting Meson Channel

Associate Professor:	H. A. Schwettman
Research Physicist:	D. P. Boyd

A superconducting pion channel has been developed and is being constructed. It consists of two, 10 ft. diameter torroidal superconducting magnets, each having 60 pancake forms. Cooling is achieved by conduction from liquid helium tubing placed on the edge of the coil forms. This novel application of large scale superconducting technology results in a large solid angle exceeding 1 steradian for the collection of pions. The purpose of the magnet is to collect and deliver pions for use in cancer therapy in a hospital facility.

(20) Time Variation of Fundamental Constants and Superconducting Cavity Stabilized Oscillator

Research Physicist: J. P. Turneaure

The investigations involve the development of an x-band microwave oscillator (called the superconducting cavity stabilized oscillator or SCSO) with state of the art short term frequency stability and the application of this oscillator in an experiment to detect possible time variation of the fine structure constant.

The technique being pursued is to reference a commercial Gunn-effect oscillator (at 8.6 GHz) to a superconducting niobium cavity. Such a cavity is an excellent frequency reference because of the very narrow resonance line-width which can be obtained. For example, an x-band niobium cavity can be made with a resonance 100 times narrower than the atomic line width of the hydrogen maser. A discriminator of the intermediate frequency type has been developed to detect the cavity resonance frequency. The improvements which we have made in both the discriminator and the servo electronics cause the cavity itself to be the dominant source of frequency instability for the entire system.

The short term frequency fluctuations of the SCSO system have been extensively studied by mixing the outputs of two identical systems and performing spectrum analysis and period-time counting on the beat signal. It has been found that the rms fractional frequency fluctuations (referred to the operating frequency) are $\sigma_y(\tau) = 6 \times 10^{-16}$ for a 100 sec averaging time. This is better than the performance of hydrogen and rubibium masers. The frequency drift of the SCSO system has also been measured via comparison with a cesium beam atomic clock for a period of about 2 weeks. The typical drift rate was 3×10^{-14} per day which is two decades lower than state of the art quartz crystal oscillators.

(21) Superconducting Microwave Cavities

Professor: H. A. Schwettman
Research Physicist: J. P. Turneaure
Research Associate: C. M. Lyneis

Several important problems have been encountered in the development of high Q, high field superconducting cavities which require a more complete understanding at a fundamental level. Investigations are in progress related to the surface resistance of superconductors, magnetic breakdown of the superconducting state, and electron loading phenomena in superconducting cavities. There are two questions related to the surface resistance of superconductors which are quite important and are currently being studied. These are the dependence of the surface resistance on material parameters such as the Landau-Ginzberg parameter, κ (the ratio of the penetration depth, λ, and the coherence length, ξ), and the electron mean free path, ℓ; and the possibility that fundamental loss mechanisms such as the generation of sound waves will set a limit on the smallest attainable surface resistance.

The maximum rf field level that can be attained in a superconducting cavity with high Q is often limited by a thermal-magnetic breakdown of the superconducting state. For high quality superconducting cavities such magnetic field limitations are characterized by an abrupt change in Q (by a factor of 10^2 and sometimes even 10^5) at a relatively well defined rf critical magnetic field, H_c^{rf}. To make progress in investigations of thermal-magnetic breakdown the superconducting surfaces must be better characterized. There are available to us a number of tools and methods to accomplish this including an Auger spectroscope, a scanning electron microscope, an electron microprobe, a transmission electron microscope, and other metallurgical equipment available at the Stanford Center for Materials Research. Also, we can utilize a number of physical measurements which help to characterize the surface including the dc resistance ratio, the normal state surface resistance, and temperature dependent surface reactance measurements.

Electron loading phenomena impose an important limitation on the field level that can be achieved in superconducting cavities at the frequencies of interest for an accelerator. At present in TM_{010} mode cavities at 1.3 GHz one is limited to electric field levels corresponding to an energy gradient of 2 MeV/ft by intense x-radiation that can exceed one R/hr measured at a distance one meter from the cavity. The observed x-radiation is thought to result from field emitted electrons, however, a detailed understanding of the phenomenon must include not only the field emission process, but also the electron dynamics in the cavity, and the secondary electron multiplication processes which follow electron impact with the cavity walls. Studies have shown that electron field emission in superconducting cavities is enhanced by geometric projections on the cavity surface and by resonant tunneling through surface states associated with adsorbed gases. Recent experiments have shown that electron dynamics and secondary processes can also have a profound influence on the electron loading in superconducting cavities. For geometrically similar cavities resonant at different frequencies the electron dynamics are invariant (all trajectories, final energies, and final phases remain unchanged) if the electric field strength is scaled with frequency. Measurements on TM_{010} mode cavities at 1.3, 2.8 and 8.6 GHz indicate that electron loading at lower frequencies becomes an important problem at electric field values that are lower, strongly suggesting that the details of electron dynamics in the cavity must be considered.

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3. S. P. Boughn, W. M. Fairbank, W. O. Hamilton, M. S. McAshan, J. E. Opfer, B. Pipes, J. M. Reynolds and R. C. Taber, "Search for Gravitational Radiation Using Low Temperature Techniques," *Experimental Gravitation*, B. Bertotti, Ed. (Academic Press, 1974) pp. 294-309.

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5. W. M. Fairbank, J. A. Lipa and C. W. F. Everitt, "The Gyroscope Experiment, 2: Development of the London-Moment Gyroscope and of Cryogenic Technology for Space," *Experimental Gravitation*, B. Bertotti, Ed. (Academic Press, 1974) pp. 361-380.

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18. ENERGY MIGRATION IN MOLECULAR SOLIDS: COHERENT VS. INCOHERENT PROPAGATION EFFECTS IN MOLECULAR SOLIDS

M. D. Fayer, Assistant Professor, Chemistry

Graduate Students:

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Agency Support

NSF through CMR
ACS--Petroleum Research Fund

Technical Objective:

To obtain an understanding of the factors affecting the migration of singlet Frenkel excitons in molecular solids. The nature of energy transport in solids is an area of great practical importance in addition to being one of the fundamental problems confronting both theoretical and experimental solid state physics. In particular, any time the collective interactions of a solid contribute to the propagation of a state or particle, both the coherent and incoherent mode of propagation must be considered in detail. This is true of singlet Frenkel excitons in molecular crystals which are the subject of this investigation but identical considerations also apply to conduction electrons in metals and insulators, electrons and holes in semiconductors, lattice or molecular vibrational energy transfer, the propagation of angular momentum in solids as spin waves or magnons and even in atomic diffusion, such as in the migration of ^3He in solid ^4He.

At low temperatures (~4° K) where phonon-exciton interactions are infrequent, wavelike propagation of coherent wave packet states is expected to be the predominant energy transport mechanism. The velocity of propagation and therefore the distances over which energy can be rapidly transported is determined by the group velocities of the individual exciton states. Increased temperature results in a greater number of excitons with large group velocities able to travel long distances, but also results in increased phonon-exciton scattering which tends to reduce the wave packets coherence length. At high temperatures, (~300° K) phonon-exciton scattering is expected to reduce the coherence length to less than one lattice site. Transport will take place by a random walk process, and therefore long range energy migration will be severely reduced. To date there is only very limited indirect experimental evidence that coherent migràtion occurs in triplet Frenkel excitons and these experiments are incapable of investigating the distances over which exciton migration occurs. Singlet Frenkel excitons which should exhibit rapid coherent migration due to their large exciton band dispersions are of particular interest because they will be able to transport energy over long distances between phonon-exciton scattering events.

Approach:

The dynamics of exciton transport in the low temperature coherent region, the high temperature random walk region and the intermediate region, are capable of being directly investigated utilizing the picosecond transient-grating technique recently developed by A. E. Siegman. In this technique, two ultra-short light pulses generated with a mode-locked laser are propagated along different paths and overlapped in the sample, i.e. a molecular crystal with a singlet absorption at the laser wavelength. The interference of the two beams produces a sinusoidally spatially varying intensity distribution in the crystal which results in the production of singlet excitons in the regions where the intensity is large. A third pulse of light from the laser (with a different wavelength) is directed into the sample at a desired time interval after the initial excitation. This probe pulse is defracted off the "grating" established by the first two pulses at a unique angle, and the intensity of the defracted beam is measured. As exciton migration proceeds, the "valleys" between the regions of high exciton concentration are filled in and the amplitude of the defracted probe pulse is reduced. Since the spatial distribution of the initial intensity is known and the time of the probe pulse is known, the rate of exciton migration can be directly measured. Detailed preliminary computer calculations indicate that the time scale of this technique is appropriate to the measurement.

Application of the transient grating technique to the exciton migration problem provides a unique tool for the study of a wide range of effects. By varying the sample temperature, the exciton and phonon population distributions are both altered. Temperature dependent velocities, coherence lengths, and phonon-exciton scattering are therefore opened to direct study. In addition, by varying the alignment of the transient grating relative to the sample crystolographic axes, the anisotropy in the directional rate of energy transport may be mapped out. This is particularly interesting in application to "one-dimensional" solids. Further, introduction of low energy impurities into the sample will localize the exciton on a particular lattice site for a period of time and therefore hinder the migration. Temperature dependent phonon interactions with these localized states will promote an excitation back into the exciton band where it will again be mobile. The concentration, temperature, and trap depth dependence of the exciton localization are also opened for study.

In addition to the transient-grating experiments, other techniques are being employed to investigate the individual processes of localization of an exciton wave packet by an impurity, promotion of a localized state to a delocalized band state, exciton-phonon scattering, the effect of high energy potential barriers on exciton migration and the transfer of excitation between unlike chromophores. The time and temperature dependence of the above processes will be investigated using a combination of temperature dependent optical spectroscopy and picosecond spectroscopy. The picosecond work employs a tunable mode-locked flash lamp pumped dye laser. A five picosecond pulse of visible light is selected from the mode-locked pulse train and is doubled into the UV. The UV pulse is then used to both excite and probe the dynamics of the above processes. The phenomena are investigated in the temperature range 1.5° K to 300° K using a variable temperature liquid helium dewar system.

Reference Publications:

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3. C. B. Harris and M. D. Fayer, "Coherent Energy Migration in Solids. II. Spin-resonance Absorption in Coherent-Wave-Packet States and the Effects of Phonon-Exciton Scattering," Physical Review B 10, 1784 (1974).

19. MACROMOLECULAR RESEARCH

P. J. Flory, J. G. Jackson-C. J. Wood Professor of Chemistry

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Agency Support:

AFOSR 73-2441-A, -2441-B
NSF DMR-73-07655 A01

Technical Objective:

To develop a better basis for understanding macromolecules and for interpreting their behavior.

Approach:

Currently, investigations are under way in the following areas:

(1) The configurational statistics of long chain molecules, and the interpretation of such properties as

spatial dimensions, dipole moments, and optical anisotropies according to rigorous principles of statistical mechanics,

(2) Rubber elasticity, the elastic equation of state including dependence on volume and temperature; theory and experiments,

(3) Strain-induced birefringence of cross-linked polymer networks,

(4) Depolarized scattering by chain molecules in relation to their structures and configurations, and

(5) Thermodynamic properties of liquid solutions with major emphasis on solutions in which at least one component is macromolecular.

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20. CUMULATIVE FATIGUE DAMAGE

Henry O. Fuchs, Professor Emeritus, Mechanical Engineering

Graduate Student:

Drew V. Nelson

Agency Support:

CMR
Association of American Railroads
Materials Engineering Department, John Deere & Co.

Technical Objective:

To develop computerized methods and general guidelines for predicting cumulative fatigue damage due to service loadings in mechanical components. These methods are intended to be more realistic and accurate than most now in use and at the same time simple enough for application by industry. Shortcuts are also being sought which will reduce test and computing time without unduly sacrificing the accuracy of fatigue life forecasts.

Approach:

Different methods of analysis have been applied to test data produced by others in a comprehensive test program conducted by several laboratories coordinated by the Fatigue Design and Evaluation Committee of the Society of Automotive Engineers.

Research Report:

This work is completed and is reported in the Ph.D. dissertation and three publications listed below. It shows that it is essential to look at fatigue failures from two different aspects. The early stage responds to local shear stresses and can be handled by relatively simple computations. The later stage responds to crack opening stresses and requires more complex computations. The second stage may be much shorter or much longer than the first, or the crack growth may even be arrested, depending on circumstances. We call the two stages initiation and propagation of cracks.

Crack Initiation

Analysis of very complex load histories by four different methods has shown that one simple approach gives results which are as good as those obtained by the most elaborate available analysis. Predictions fall within the usual scatter band of test results. The simple approach is based on load histories abbreviated to include only the top decile of all overall load ranges (Ref. 1). The load ranges are converted to nominal stress ranges. Damage for each range is computed as the inverse of life on an a-priori stress-life curve. Life as a function of nominal stress on the notched member is derived from the stress-life curve of smooth specimens by using the theoretical stress concentration factor at a million reversals, no notch effect at 1000 reversals, and notch strengthening at very short lives as indicated by a straight line on a log log plot through the point at 1000 and at 1 million reversals. The notch strengthening at short lives is a feature which contradicts some current theories but has long been assumed by practitioners. We are at present checking the notch strengthening in monotonic loading for these materials.

The Association of American Railroads is incorporating the method developed in this project into their fatigue design specifications for freight cars.

Crack Propagation

Three methods were tried to correlate the observed crack growth resulting from irregular load histories with data from constant amplitude tests.

The results are not quite as good as those for crack initiation, but they are very promising. We plan to do further analytic work on this problem if we can find the necessary funding.

Reference Publications:

(1) "Shortcuts in Cumulative Damage Analysis," by H. O. Fuchs, D. V. Nelson, M. A. Burke, and T. L. Toomay, SAE paper No. 730565, May 1973.

(2) Predictions of Cumulative Fatigue Damage Using Condensed Load Histories, D. V. Nelson and H. O. Fuchs.

(3) Review of Fatigue Crack Growth Prediction under Irregular Loading, D. V. Nelson. Presented to Society for Experimental Stress Analysis on 13 May, 1975, Chicago.

(4) Prediction of Fatigue Crack Growth under Irregular Loading by D. V. Nelson and H. O. Fuchs. Accepted for presentation at American Society for Testing and Materials Symposium on Fatigue Crack Growth under Spectrum Loads, on 24 June 1975 in Montreal.

21. LOW TEMPERATURE PROPERTIES OF MATERIALS

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R. G. Younge

Agency Support:

AFOSR 73-2435B
NSF DMR74-21982
NSF through CMR

Technical Objective:

To prepare new and unusual superconducting and magnetic compounds and composite structures and to study the mechanisms and interactions responsible for their behavior.

Approach:

Techniques such as vapor transport, electron-beam evaporation, arc melting, powder metallurgy, and electrolysis are used to prepare crystals, compounds, or materials of interest. Their electronic properties are then correlated with their structural properties by investigating superconducting transitions, heat capacities, optical and transport properties.

Research Report:

(1) Transition Metal Dichalcogenides

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Professional Associates:

K. R. Pisharody
R. E. Schwall

Studies have been made of the changes in superconducting transitions in the layered structures in response to physical and chemical variables. Pressure experiments were carried out (in collaboration with T. F. Smith and P. N. Shelton) as a function of stoichiometry in $NbSe_2$ in order to study the relationship between layer spacing, T_c, and crystal perfection. A large initial increase of T_c was observed for the samples studied containing up to 10% excess Nb, indicating that the large initial dT_c/dp ($\sim 5 \times 10^{-5}$ $Kbar^{-1}$) is not merely due to the suppression of a charge density wave. Chemical studies using interaction of H, carried out in collaboration with Di Salvo and Murphy at Bell Labs, indicate that suppression of the charge density wave state in $NbSe_2$ raises T_c by the order of 0.2°K vs 3°K for TaS_2.

Reference Publications and Presentations:

"Properties of H_xTaS_2 : Correlation between the Superconducting T_c and Electronic Instability in Layer Compounds," by D.W. Murphy, F.J. Di Salvo, G.W. Hull, Jr., J.V. Waszczak, S.F. Meyer, G.R. Stewart, S. Early, J.V. Acrivos, and T.H. Geballe, J. Chem. Phys. 62, 967 (1975).

"Insertion Compounds of $2H\text{-}TaS_2 \cdot NH_3$," by S.F. Meyer, J.V. Acrivos, and T.H. Geballe, Proc. Natl. Acad. Sci. USA 72, 464 (1975).

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"Rate of Intercalation of Transition Element Dichalcogenides," by J.R. Salem and J.V. Acrivos, Bull. Am. Chem. Soc.

"Superconducting Critical Fields of TaS_2 and $TaS_{1.6}Se_{0.4}$ Organic Intercalation Compounds," by D.E. Prober, M.R. Beasley, and R.E. Schwall, Bull. Am. Phys. Soc. 20, 342 (1975).

(2) Non-A15 Structures and Polymers

Graduate Students: J.M.E. Harper
G. R. Stewart
B. Robinson

Professional Associates:

C. N. King
J. M. Rowell

A sensitive diamond calorimeter has been developed that is capable of measuring absolute heat capacities of small (~ 10 mg) samples up to ~ 50°K . The heat capacity apparatus has been interfaced with a computer in a way that permits the pulsed, or ac sweep method to be used. A study of the heat capacity of SN polymers (superconducting below 1°K), in collaboration with R. L. Greene of IBM, in the temperature range above 1°K showed modes characteristic of one-dimensional vibrations. Work on MnBi , in collaboration with Stutius, White, and Chu of Xerox, has shown that the density of states at the Fermi surface is extremely small, more like a semiconductor than a metal. High pressure studies of tetrahedrally bonded $CuCl$, in collaboration with C. W. Chu of Cleveland State, has uncovered an insulator-metal-insulator sequence of phases at room temperature. The implications of these results with respect to covalent, metallic and ionic bonding, as well as the metallic behavior at low temperatures, are of interest.

An apparatus has been developed to measure the low level dielectric losses ($\tan \delta \sim 10^{-7}$ to 10^{-4}) that occur in polymers at cryogenic temperatures. We have determined the magnitude of the losses characteristic of the various polymer types. We have made a concerted effort to distinguish the "impurity" losses from the intrinsic losses in polyethylene and, in so doing, we have identified the effects of certain additives frequently found in commercial polyethylene.

The high vacuum equipment allowing evaporation onto a substrate at temperatures < 2°K , which was used previously for measurement of T_c of amorphous transition metals, was adapted so that tunnel junctions of the type aluminum-aluminum oxide-transition metal could be prepared. Initial interest is in Mo and Nb . The tunneling characteristic for Al-oxide-Nb junctions shows clearly the effect of annealing of the Nb film, in that structures due to phonons of the crystalline state become stronger with annealing to higher temperatures (50 - 250°K).

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"Electronic Structure of MnBi ," by W. Stutius, R.M. White, T. Chen, and G.R. Stewart, in Proceedings of 20th Annual Conference on Magnetism and Magnetic Materials (in press).

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(3) A15 Synthesis and Properties

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Professional Associates:

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This family comprises all the known high temperature superconductors. The synthesis of various members by means of independently controllable electron beams has been shown to be highly controllable insofar as stochiometry and texture are concerned. Single-layered and multilayered Nb_3Sn tubes have been prepared in order to study dissipative processes which occur during current flow. Ac losses and critical currents have been measured up to 14°K and are being correlated with surface properties, film thickness and other parameters.

Reference publications and presentations:

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"Low Temperature Thermal and Electrical Properties of Chemical-Vapor-Deposited Nb$_3$Ge ," by J.M.E. Harper, T. H. Geballe, L.R. Newkir, and F.A. Valencia, J. Less-Common Metals (in press).

"Evaluation of Layered Nb$_3$Sn Conductor," by R.E. Schwall, R.E. Howard, and R.B. Zubeck, IEEE Trans. Mag. MAG-11, 397 (1975).

"Electron Beam Evaporation Synthesis of A15 Superconducting Compounds: Accomplishments and Prospects," by R.H. Hammond, IEEE Trans. Mag. MAG-11, 201 (1975).

"Critical Currents in Thin Film Nb$_3$Sn ," by R.E. Howard, R.B. Zubeck, and R.E. Schwall, Bull. Am. Phys. Soc. 20, 294 (1975).

22. SUPERCONDUCTING POWER TRANSMISSION LINE MATERIALS RESEARCH

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Agency Support:

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EPRI/ERDA E(49-18)-1569

Technical Objectives:

To produce prototype conductors for potential use in superconducting power transmission lines which demonstrate the technical and economic feasibility of using superconductors in underground power transmission.

Approach:

Emphasizes research for new superconducting materials and new methods of incorporating superconductors into practical cables with all the desired properties. Focus is presently on multilayered composites of Nb_3Sn and normal metal (pinning) barriers. Fabrication of the conductors is accomplished using dual electron beam codeposition on hot substrates. Critical currents and ac losses of conductors are measured.

Research Reports:

(1) Conductor Fabrication

We have been exploring in detail the materials science of the electron beam vacuum deposited films of Nb_3Sn which are of critical importance in our layered composites. We had shown earlier that excellent compositional control was routinely possible and that material with good transition temperature, critical currents, and low ac losses could be produced with our system. We were concerned, however, with the surface quality and growth morphology, as these should directly affect the loss performance and also our ability to produce well-defined layers in our composite. The results of our surface quality studies have been very successful. We have found that very good surfaces and growth morphologies can be obtained under optimal depsoition conditions which appear to be located in a narrow substrate temperature window near 650°C . Also, and very importantly, we have found that the observed behavior of our surfaces under different deposition conditions can be largely understood on the basis of recent fundamental work on the surface and growth morphologies of vacuum deposited thin films. As a result, our efforts now have a firmer scientific base and need not be so empirical.

Reference Publications and Presentations:

R. H. Hammond, "Electron Beam Evaporation Synthesis of A15 Superconducting Compounds: Accomplishments and Prospects." IEEE Trans. Mag. MAG-11, 201 (1975).

NSF-RANN Semiannual Progress Report, "Superconducting Power Transmission Lines," M.L. Report No. 2441 (Stanford University).

(2) Critical Currents and AC Losses

A new extremely sensitive electrical scheme for measuring low ac losses in superconductors has been developed. Losses measured with this instrument have been found to be in agreement with losses measured earlier using a calorimetric method. Losses sufficiently low for power line applications have been demonstrated, even for temperatures above 4.2°K in our layered composites. A nearly universal temperature dependence $[J_c \propto (1-(T/T_c)^2)]$ has been observed in our samples, which suggests a simple interpretation of the flux pinning mechanism involved may be possible.

Reference Publications and Presentations:

R. E. Schwall, R. E. Howard, and R. B. Zubeck, "Evaluation of Layered Nb_3Sn Conductor," IEEE Trans. Mag. MAG-11, 397 (1975).

R. E. Howard, R. B. Zubeck, and R. E. Schwall, "Critical Currents in Thin Film Nb_3Sn ." Bull. Am. Phys. Soc. 20, 294 (1975).

NSF-RANN Semiannual Progress Report, "Superconducting Power Transmission Lines," M.L. Report No. 2441 (Stanford University).

23. ION IMPLANTATION IN SEMICONDUCTORS AND PROTON-ENHANCED DIFFUSION

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Technical Objective:

Research effort in the ion implantation group at Stanford is presently centered around four major topics: ion implantation and proton-enhanced diffusion in elemental and III-V compound semiconductors; improved computations of range and damage statistics for implanted ions; and ion implantation in CdTe.

Research Report:

(1) Investigation of Proton-Enhanced Diffusion Mechanisms for B in Si and SiO_2

Graduate Student: J. Ross Anderson

There are two purposes in this research. The first is to more fully characterize proton-enhanced diffusion (PED) than has been done previously, by measuring impurity profiles after PED at various temperatures, current, and lengths of time. This will be important to those using PED to make devices.

The second purpose is to try to use these and other data to determine how protons enhance the diffusion of impurities in silicon. In the past it has been assumed that vacancies created by the proton bombardment are responsible for diffusion enhancement, but actually proton bombardment also produces interstitials and electron-hole pairs and perhaps more complicated defects such as divacancies, all of which may affect diffusion.

To date our work has been with boron-doped silicon, and some comparisons have been made with Nelson's experiment of PED in boron doped silicon [1] and Minear's theory of PED [2].

Our main results are as follows. If boron-doped silicon is bombarded by 10 kV protons at 550°C, no significant PED occurs, though damage is introduced. The electrical effect of the damage is that approximately one carrier is lost per proton; that is, the electrical activity of one boron atom is lost for each injected proton. This is not a chemical reaction between the proton and the boron because a 10 kV helium atom, which is heavier than a proton and thus causes more damage, causes the loss of approximately 8 carriers. Hence we conclude that the loss of electrical activity is associated with the formation of boron-vacancy complexes.

The damage produced by either protons or helium atoms at 550°C is very stable; its anneal has an activation energy of 4.4 eV, as compared to about 3.1 eV for diffusion. The metallurgical characteristics of this damage are being studied with transmission electron microscopy.

In contrast to these results, the bombardment of boron, phosphorous, or arsenic-doped silicon by protons at temperatures of 750°C or greater will produce significant PED. All three diffusivities are enhanced by approximately the same factor relative to their thermal diffusivities. This would appear to rule out interstitial diffusion of boron or phosphorous in silicon because it is unlikely that interstitial diffusers would be enhanced by the same factor as substitutional diffusers such as arsenic.

As in the damage case, there is evidence that 10 kV protons interact with dopants in approximately a 1:1 ratio. Furthermore, since vacancies must be involved in the diffusion process, all of the results given above can only be interpreted by assuming that vacancy-impurity pairs must be the diffuison species.

These observations have led to a new mathematical model of thermal diffusion involving impurity-vacancy pairs which will soon be published. This model shows that for standard thermal diffusion of boron from a constant source, the impurity distribution takes the form of the square root of an error function at high concentrations, and at low concentrations it takes the form of an error function. This is in good agreement with experimental results that have been previously unexplained [3]. Application of the model to the process of proton-enhanced diffusion is being explored.

References

1. Daniel G. Nelson, "Radiation Enhanced Diffusion of Boron in Silicon," Ph.D. Thesis, Stanford University, March 1970.
2. Roger L. Minear, "Diffusion Enhancement in Germanium by Light Ion Implantation," Report No. 4725-1, Stanford Electronics Laboratories, Stanford University, March 1970.
3. M. Okamura, Jap. J. Appl. Phys. Vol. 8, 1440 (1969).

(2) Ion Implantation in Cadmium Telluride

Graduate Student: John C. Bean

The purpose of this project is to determine whether arsenic and other dopants may be introduced into CdTe with low enough residual damage and high enough doping efficiency to facilitate construction of gamma ray detectors and heterojunction solar cells. Samples are evaluated via resisitivity and Hall effect data in the temperature range of 77 to 400°K, and by transmission electron microscopy.

In the first year of this work a method was developed for preparing CdTe for microstructural analysis in the transmission electron microscope. This technique was used to explore as-grown crystal quality, the effects of various vapor annealing steps and the effects of ion irradiation. Using this data and the results of resistivity and Hall effect measurement, a pre- and post-implantation annealing schedule was found which would result in near 100% implanted arsenic ion electrical activity.

In the second year of this project, we have continued our efforts to find the optimum heat treatment steps for arsenic ion implantation. In addition, implantations have been done using boron nitrogen, phosphorous, and antimony ions. A technique for the anodic oxidation of CdTe has been developed allowing for the accurate sectioning of CdTe to a resolution of approximately 1000 Å. This technique has been used to determine doping profiles in phosphorous implanted samples.

The most significant finding of the last years work has been of the signifcant batch-to-batch quality variations in CdTe available from commercial sources. These variations have been documented using transmission electron microscopy, infrared and optical microscopy and laser calorimetry. In many cases, material quality has completely masked the effects of ion implantation.

To circumvent the extreme dependence of our results on material quality, we are building apparatus to permit epitaxial growth of CdTe, which we hope will provide a controlled substrate for subsequent ion implantation.

(3) Proton-Enhanced Diffusion of Cd in InSb

Graduate Student: Cheol K. Kim

Due to surface decomposition and hillock formation during thermal diffusion, it is extremely difficult to produce high quality pn junctions in indium antimonide (InSb). This difficulty arises from the requirement that the sample should be held at elevated temperatures for a substantial period of time for the diffuison of the impurity to occur. It is therefore interesting to investigate proton-enhanced diffuison (PED) as a means to introduce impurities at lower temperature.

To perform a proton-enhanced diffusion it is first necessary to establish

1. A means of preparing the desired dopants without introducing excessive damage into the host crystal;

2. An upper target temperature which the host crystal can stand in a vacuum system without decomposing (this temperature will in general depend on the nature of any coating that may be applied to the sample surface and the proton flux to be applied in the course of PED); and finally

3. A maximum proton flux that can be injected into the sample such that enhanced diffusion can occur with either no residual damage or such light residual damage that a post-PED anneal can be used to return the crystal to an essentially defect-free state.

The research described here was undertaken to determine a set of answers to these questions for the introduction of Cd into InSb, a process that is of general interest for the fabrication of infrared detector diodes. The three main questions listed above were answered affirmatively as follows:

1. Successful thermal predeposition of Cd in InSb was done without the formation of hillocks by developing a new source: 45-55 atomic percent cadmium antimonide alloy. Using this source, a junction depth of 0.3 micron was obtained following diffusion at 380 degree centigrade for 3 hours. The best fit erfc curve on the experimental data indicates that the surface density of Cd is 4.55 x 10^{20} per cubic centimeter with the Hall mobility 500 cm^2/volt-second. Analysis shows that there are nonactive atoms near the surface. A possible dependence of diffusivity on the density of Cd is also observed during the shallow diffusion.

2. A series of vacuum heating experiments was performed to determine the maximum temperature that an InSb sample can withstand without surface decomposition. The experimentally determined maximum temperature for an uncoated sample was 360°C.

3. A series of proton flux vs energy experiments was performed and a line in the flux-energy plane was determined which divides the plane into two regions. In one of these regions bombardment-produced damage is essentially fully annealed, while in the other it is not. The approximate equation for this line is: J is equal to 2400 divided by E_0 where J is the proton current density in nanoampere per square centimeter and E_0 is the proton energy in kiloelectron volt.

The particular experimental conditions employed for most of the proton-enhanced diffusion experiments reported here were as follows. Cd was thermally predeposited in the manner described in 1 above. A predeposited sample was then mounted in a sample holder with half of the sample masked with a molybdenum plate, after which this sample was loaded on the target chamber of a 150 keV ion implantation system. PED was then performed at a sample temperature of 360°C and 10^{-6} Torr vacuum at various proton energies and fluxes. High electric activity of the diffused Cd was successfully observed only by annealing the PED sample in an evacuated ampoule at 400°C for 2 hours. A possible explanation for this observation is that Cd diffused during PED forces In to locate at an interstitial site. However, during the annealing period the interstitial In appears to either move out toward surface or get trapped in a vacancy or dislocation in the bulk.

(4) Range and Damage Profiles for Ions Implanted by a Knock-On Process

Graduate Student: David Smith

The purpose of this project is to apply the general LSS formalism for range computations to the problem of estimating the range and damage distributions of knock-ons. A problem of particular importance is the following. When ions are implanted through a thin layer of SiO_2, some energetic Si^+ and O^+ ions are produced which may then be implanted into the underlying substrate. The number of O^+ ions knocked on is of particular interest since oxygen is known to form deep trapping centers in silicon, and therefore the properties of pn junctions in the vicinity of the knocked-on oxygen atoms will be deteriorated.

A model for calculating the distribution of knock-ons has been developed and applied to the case of 150 keV As ions implanted into Si through a 500 Å SiO_2 mask. It has been found that about 2 oxygen atoms are knocked into the Si for each implanted As atom; and that a significant number of oxygen atoms can be found at depths as great as 1000 Å below the SiO_2-Si interface.

Experimental apparatus is being constructed to measure the distribution of knocked-on ions. The experimental distribution will be correlated with theory and improvements will be made as necessary to produce a reasonable basis for calculating the knock-on ion distribution for cases of practical interest.

(5) Ion Implantation and Radiation-Enhanced Diffusion of Zn in $GaAs_xP_{1-x}$

Graduate Student: Edward B. Stoneham

Control over the diffusion rate of ion-implanted zinc in gallium arsenide phosphide has been achieved through the use of multiple implants in which some gallium arsenic, or phosphorous is co-implanted with the zinc prior to annealing and diffusion. A substantial amount of data obtained through new experimental techniques is presented to characterize this method of diffusion control, and a model is developed to explain the results.

Samples of n-type epitaxial gallium arsenide phosphide were implanted at room temperature with zinc at doses between 10^{14} and 10^{16} cm^{-2} and with various amounts of gallium, arsenic, and phosphorus. All ion energies were chosen to give a projected range of 270 Å. The samples were coated with silicon nitride as an encapsulant and were annealed in sealed, evacuated quartz ampoules at temperatures between 750° and 900°C, causing the implanted zinc to diffuse to several times its initial depth. The development of a new anodic oxidation method made possible rapid and accurate measurements of the diffusion depth and the conductivity, mobility, and carrier concentration profiles of the shallow zinc-diffused layers.

It was found that the co-implantation of arsenic or phosphorus greatly inhibits the diffusion of the zinc while gallium co-implantation tends to enhance it. A nine-to-one range of junction depths in samples implanted with a constant zinc dose and annealed at 850°C for one hour was achieved through appropriate co-implantations of gallium or arsenic. The degree to which zinc diffusion could be inhibited by arsenic co-implantation was found to be limited, with no significant changes occurring beyond a certain arsenic dose.

The results are explanible in terms of the interstitial-substitutional theory of zinc diffusion for which a comprehensive review is given. The diffusion coefficient is inversely proportional to the gallium vacancy concentration which, in turn, is determined by the initial stoichiometry of the material and the stoichiometry of the implanted layer. Arsenic or phosphorous co-implantation increases the gallium vacancy concentration near the surface, thereby decreasing the zinc diffusion coefficient. The degree to which diffusion can be inhibited is limited by thermodynamic restrictions on the range of gallium vacancy concentrations that can exist at equilibrium in the material at a given temperature.

Also discussed are transmission electron microscopy results which indicate that arsenic precipitates near the surface during annealing when enough arsenic has been co-implanted with zinc to fully inhibit the zinc diffusion. Measurements of light emitting diode characteristics are presented to show that arsenic co-implantation can produce significant improvements. The results of attempts to alter the diffusion rate of zinc by proton bombardment or low-energy electron bombardment are also presented.

Finally, some important practical applications and general implications are discussed, and suggestions for future research are offered.

(6) Proton-Enhanced Diffusion in GaAs

Graduate Student: Robert E. Tremain, Jr.

The general objective of this project is to develop proton-enhanced diffusion as a process for introducing thin, doped layers into GaAs. Dopant elements being studied are Si, S, Se, Te, Zn, and Cd. The project is motivated by the need for thin, highly-doped surface layers for use in high-frequency transistors, as well as bipolar transistors and even simply contacting GaAs in cases where that is now difficult. Since proton-enhanced diffusion is a relatively low temperature process, and since unique doping profiles can be obtained, the process appears to be well suited for these purposes.

Our previous work on the PED process in GaAs shows that S, Se, and Cr can be successfully diffused, but electrical activity of the diffused dopant still appears to be low. Therefore, we have undertaken a study of the effects of degeneracy on the implantation-doping of GaAs and have found that a large variety of experimental results in GaAs, including every known method of doping, can be explained by a careful analysis of the effects of degeneracy on apparent doping efficiency. An initial paper describing this effect has been published and a more detailed investigation which includes energy band modifications is being developed.

Publications

1. "The Effects of Ion-Implanted Ga, As, and P on the Subsequent Diffusion of Ion-Implanted As in $GaAs_{0.6}P_{0.4}$," E. B. Stoneham and J. F. Gibbons, Proceedings of the 4th International Conference on Ion Implantation in Semiconductors, Osaka, Japan (August 1974).
2. "The Effects of Non-Gaussian Range Statistics on Energy Deposition Profiles," S. W. Mylroie and J. F. Gibbons, Proceedings of the 4th International Conference on Ion Implantation in Semiconductors, Osaka, Japan (August 1974).
3. "The Effects of Degeneracy on Doping Efficiency for n-type Implants in GaAs," J. F. Gibbons and R. E. Tremain, Jr., Appl. Phys. Letters 26, 199 (February 1975).
4. Projected Range Statistics in Semiconductors, J. F. Gibbons, W. S. Johnson and S. W. Mylroie, Dowden, Hutchinson & Ross, Publishers, (Stroudsburg, Pennsylvania) 1975.

24. MÖSSBAUER EFFECT AND RELATED PHENOMENA

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Agency Support:

NSF GP 37106 A1
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Technical Objective:

To use the Mössbauer effect and perturbed angular correlations to study solid state, atomic, and nuclear phenomena: in particular hyperfine interactions, ion implantation phenomena, atomic interactions in solids and nuclear moments and polarizations.

Approach:

Nuclear moments of very short lived states are measured by use of hyperfine fields in atoms and ions. New techniques for the measurement of moments of long lived states are being used Polarized targets are produced by low temperature orientation techniques for studies in nuclear physics. Solid state phenomena are being investigated with the Mössbauer effect at very low temperatures by means of a dilution refrigerator. The structure of amorphous compounds and electronic densities at the nucleus in crystals are also being studied by means of Mössbauer measurements.

Research Report:

(1) Magnetic Hyperfine Structure in the Mixed-Valence Compound TmSe

The concept of rapid valence fluctuations between two distinctly different 4f electronic configurations has been recently advanced as an explanation for the demagnetization of rare earth ions in dilute alloys and some intermetallic compounds.[1,2] X-ray photoemission experiments have shown two simultaneous 4f multiplet structures corresponding to the daughter configurations and have been interpreted as direct evidence[3] for the existence of interconfiguration fluctuations (ICF). The cubic intermetallic compound TmSe which has a well characterized mixed valence state[4] exhibits magnetic order and is one of the materials in which photoelectron evidence for ICF (involving Tm^{3+} and Tm^{2+}) has been reported.[3] We are investigating the hyperfine structure in TmSe detected "nondestructively" by means of the Mössbauer effect of ^{169}Tm ($E = 8.4$ keV, $\tau = 3.5$ nsec, $3/2 \leftrightarrow 1/2$ transition). Mössbauer spectra, taken with a single-line source of ^{169}Tm and an absorber prepared by powdering a single crystal of TmSe, show a 6-line magnetic pattern below T = 2 K. All of these spectra can be approximately fitted with a single hyperfine field of 1.93 ± 0.02 MOe (about 27% of the Tm^{3+} free ion hyperfine field) and a quadrupole interaction of $\frac{1}{4} e^2qQ = 1.2 \pm 0.02 \times 10^{-7}$ eV (about 6% of the free ion value for Tm^{3+}). The nuclear polarization observed in the spectra taken near 0.05 K is consistent with the measured temperature.

The Tm^{3+} and Tm^{2+} ground multiplets are $^3H_6$ and $^2F_{7/2}$, respectively. The magnetic dipole and electric quadrupole hyperfine interactions of these multiplets were calculated by diagonalizing the cubic crystal field Hamiltonian in the presence of an exchange field projected onto the spin of the multiplet. The results were used to contract theoretical Mössbauer spectra for the two fluctuating configurations Tm^{3+} and Tm^{2+}. Two 6-line patterns of ^{169}Tm are obtained in the slow relaxation limit, $\tau > 10^{-8}$ sec, corresponding to the two hyperfine fields calculated for the 2+ and 3+ states of 2.29 MOe and 1.68 MOe, respectively. As the mean lifetime of the fluctuating states decreases, the hyperfine spectra assume a shape rather similar to the fast relaxation limit, $\tau < 10^{-10}$ sec, which is a single 6-line pattern with the appropriate hyperfine parameters which are the average of those for the slow relaxation spectra. The calculated spectrum for $\tau = 3.5 \times 10^{-10}$ sec is in rather good agreement with the experimental spectra. Hence, we conclude that, if the low-temperature properties of TmSe are interpreted in terms of an ICF model, the characteristic fluctuation time is of the order of 10^{-10} - 10^{-9} sec.

(2) Hyperfine Studies by Use of Polarized Reactions

A new method for studying hyperfine interactions has been developed in which polarized nuclei are produced from nuclear reactions initiated with fast polarized beams of protons and deuterons. We have demonstrated that in these reactions the net polarization transferred to all residual nuclei is large enough to make possible quantitative studies of nuclear polarization and moments.

As examples of the process, the β-emitting nuclei ^{8}Li, ^{12}B and ^{29}P have been produced and polarized by $(\vec{d},p)$ and $(\vec{d},n)$ reactions with the deuteron beam polarized perpendicular to the beam direction. The targets were Li metal, ZrB_2 and Si crystals, respectively, thick enough (100 mg/cm^2) to stop both the beam and all the recoil nuclei. The polarization transferred to the recoil nuclei was measured by detecting the resulting β asymmetries. Since all recoil nuclei are used, high β counting rates of $10^{3} \rightarrow 10^{4}$ cps were obtained in two particle telescopes placed at 0 and 180° to the polarization direction. The incident beam was pulsed and β particles were counted only during the period between pulses. To eliminate possible instrumental asymmetries, counts were accumulated with the beam polarization alternately on and off. For the reactions $^{7}Li(\vec{d},p)^{8}Li$ and $^{11}B(\vec{d},p)^{12}B$ the net polarization transferred to all residual nuclei (with a beam polarization $P_z = 0.6$) produced an up-down asymmetry of about 9% in the β-decay, which is fairly independent of energy for the thick targets used. It is interesting that in the case of $^{28}Si(\vec{d},n)^{29}P$ the polarization transferred was found to be opposite (and smaller) than in the other examples. This polarization transfer mechanism has also been observed in the reactions $^{31}P(\vec{p},n)^{31}S$ and $^{39}K(\vec{p},n)^{39}Ca$ in thick targets of P_4S_7 and $KCaF_3$. With the proton beam, measurements could be made with spin up and down.

The polarized nuclei produced by this technique have been used to study nuclear-spin relaxation phenomena and to measure nuclear moments by means of NMR detection.[5] In the case of ^{12}B for which the nuclear moments are known, an NMR measurement was carried out as a test of the method. The resonance observed confirmed all aspects of the method.

A preliminary NMR measurement has been carried out on ^{39}Ca to measure its magnetic moment and ultimately its quadrupole moment. Since the observed asymmetry was small very precise measurements will be needed to obtain the lineshape of the resonance and hence a precise value of the magnetic moment and the quadrupole coupling. From the location of the resonance, however, a value of 0.94 ± 0.03 has been derived for the magnetic moment of ^{39}Ca.

In order to measure the quadrupole moment of ^{8}Li ($I^{\pi} = 2^{+}$, $T_{1/2} = 0.84$ sec) the recoil nuclei were implanted in a thick target of $LiIO_3$ (hexagonal single crystal). A holding field H_o of 1.63 kG was applied along the polarization direction to preserve the nuclear polarization. The asymmetry in the β-decay from the polarized ^{8}Li was measured as a function of time following each pulse so as to measure the spin-lattice relaxation time T_1. The initial asymmetry was determined to be 0.035 ± 0.002 with a relaxation time of $T_1 \approx 11$ sec which is much longer than the half-life of ^{8}Li. The large value of T_1 demonstrated the usefulness of the $LiIO_3$ crystal for recoil implantation. The initial ^{8}Li polarization measured in $LiIO_3$ was about 1/3 of that measured in Li metal. This suggests that 1/3 of the recoils find substitutional Li sites, where the electric field gradient is known to be axially symmetric in a direction parallel to the crystal c-axis.[6] To measure the quadrupole moment of ^{8}Li[7] an rf magnetic field was applied perpendicular to the holding field which served as the NMR field H_o. If a "small" quadrupole interaction is present in addition to the "large" magnetic interaction with H_o, one expects to observe four resonances of slightly different frequencies. These four resonances were detected by scanning with the rf frequency, while the other three transitions were saturated by modulated rf signals. At the center of each resonance the polarization was completely destroyed when the other transitions were saturated. This result shows that the nuclear spin is I = 2, that the field gradient is unique, and that the ^{8}Li nuclei which keep their polarization sit in equivalent sites in the LiIO$_3$ crystal. The intrinsic line broadening obtained from the line-shape analysis was consistent with the dipolar broadening estimated for ^{8}Li in this crystal. Thus, broadening produced by radiation damage was small, although it was shown that a holding field greater than about 1 kG was necessary to decouple the time-dependent interactions which are due presumably to radiation damage. The electric quadrupole coupling constant of ^{8}Li in LiIO$_3$, as determined from the resonant frequencies, is $|eqQ| = 29.2 \pm 0.8$ kHz. Using the known[6] coupling constant of ^{7}Li, we obtain the ratio of ground state quadrupole moments

$$Q(^8\mathrm{Li})/Q(^7\mathrm{Li}) = 0.66 \pm 0.05$$

in fair agreement with the result obtained using polarized neutron capture by Ackerman et al.[7]

(3) Decoupling of the Hyperfine Interactions in ^{40}Ca Ions Recoiling in Vacuum

The study of hyperfine interactions in highly ionized ions has been continued. The work has concentrated on the hyperfine interaction in ^{40}Ca ions produced in a nuclear reaction and recoiling into vacuum at a velocity $v/c = 1.45\%$. The method makes use of a strong magnetic field along the beam axis to decouple the nuclear and electronic angular momenta. The 3.74 MeV (3^-, $\tau = 61$ ps) state in ^{40}Ca, used as a probe of the hyperfine interaction, was populated through inelastic α-scattering, $^{40}\mathrm{Ca}(\alpha,\alpha')^{40}\mathrm{Ca}^*$, at an incident α-energy of 16.17 MeV. This energy produced an adequate cross-section at backward α-angles for the production of the 3^- state, while minimizing the yield of the neighboring 2^+ state. Backscattered α-particles were detected in an annular detector. Two superconducting coils with a one inch gap produced fields at the target up to 34 kG. The 3.73 MeV γ-rays were detected at 30° and 60° in coincidence with the α-particles. The detector at 30° was a 5" × 6" NaI(Tl) and the one at 60° a 10" × 10" NaI(Tl) detector. Sheets of Fe-Si were used to shield the NaI(Tl) detectors from the strong magnetic field. The targets made of natural calcium 200 $\mu g/cm^2$ thick were evaporated on a formvar backing 3 $\mu g/cm^2$ thick. The ratio of α-γ coincidences at 30° and 60°, i.e. $W(30°)/W(60°)$ was measured as a function of the external magnetic field. The ratio changed rapidly with applied field, indicating that the nuclear spin was being decoupled from the atomic hyperfine field.

The α-γ angular correlation is given by

$$W(\theta) = \sum_{k,k'} A_k^{\alpha} A_{k'}^{\gamma} G_{k,k'} P_{k,k'}(\cos\theta)$$

where $G_{k,k'}$ are the attenuation coefficients which depend on the Hamiltonian $\mathcal{H}$. For each value of the applied decoupling field H_{ex}

$$\mathcal{H} = a\vec{I}\cdot\vec{J} + bm_J - cm_I$$

where $b = g_J \mu_B H_{ex}/J$, $c = g_n \mu_n H_{ex}/I$, and $a\vec{I}\cdot\vec{J} = \vec{\mu}_I \cdot \vec{H}_{hf}$. The hyperfine field H_{hf} can be calculated for a given electronic configuration if the electronic orbitals are known. The significant quantities $\Psi(0)$ and $\langle 1/r^3 \rangle$ were obtained by Hartree-Fock calculations using the Herman-Skillman program.[8] A phenomenological correction of 10% was applied to s-fields and a relativistic correction of 4% to the p-fields. The charge state distribution for the recoiling ions was obtained from the formula of Betz et al.[9] For Ca ions with $v/c = 1.45\%$ we obtained $F(2) = 0.025$, $F(3) = 0.159$, $F(4) = 0.374$, $F(5) = 0.324$, $F(6) = 0.106$, $F(7) = 0.012$. To obtain the distribution of electrons over the various orbitals we assume: (1) $n = 1$ and 2 electron shells are not disturbed, i.e., they are filled up via optical transitions in a time $t << \tau$ the nuclear lifetime, (2) the remaining electrons are statistically distributed over $n = 3$ and 4 and the 5s-shell. With these assumptions one can calculate the probability $P_{n\ell}(q,n)$ for n electrons in quantum state $(n\ell)$ in charge state q.

Combining it with the charge state distribution we get

$$F_{n\ell}(n) = \sum_q F(q) P_{n\ell}(q,n)$$

for the fraction of ions with n electrons in quantum state $(n\ell)$. We now assume (i) that only 3s, 3p and 4s electrons produce appreciable perturbations and (ii) that there is no interaction between different electronic subshells, i.e., the hyperfine fields due to 3s, 3p or 4s electrons can be treated independently. From these considerations we obtain the results in the table.

Configuration	Term	Probability	H_{hf}(MG)
3s	$^2S_{1/2}$	0.20	21.9
4s	$^2S_{1/2}$	0.20	6.0
3p	$^2P_{3/2}$	0.27	2.9
	$^2P_{1/2}$	0.14	5.0
$(3p)^2$	$^1D_2$	0.04	14.8
	$^3P_2$	0.04	4.0
	^1S_o		0

The attenuation coefficients G_{kk} are calculated for each term and a weighted average is obtained. The ratio W(30°)/W(60°) is then constructed and fitted to the experimental points for various values of the g-factor of the 3^- state of ^{40}Ca. The best fit is obtained for g = 0.60. The value of $g \approx 0.60$ for the 3^- state is in agreement with the theoretical value g = 0.55 obtained from a particle-hole configuration of the type $f_{7/2}d^{-1}_{3/2}$.

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25. GENERATION OF ULTRAVIOLET AND VACUUM ULTRAVIOLET RADIATION

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Graduate Students:

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M. D. Wright

Agency Support:

NASA NGL-05-020-103
NAVY N00014-75-C-0576
ARMY DAHC04-74-C-0033
AF F19628-75-C-0046
AEC LLL-8532009
AEC LASL XP5-82466-1
ARPA through CMR

Technical Objectives:

To develop techniques for producing tunable coherent radiation in the ultraviolet, vacuum ultraviolet, and soft x-ray regions of the electromagnetic spectrum. Other projects, including efficient up-conversion of infrared images with metal vapors, are underway.

Research Report:

Work continues on an AEC-supported program to obtain high conversion efficiency from 1.06 μ to 0.3547 μ. Conversion efficiency in mixtures of metal vapors and inert gases has thus far been limited to about 10%. This limitation results from condensation of the hot metal vapor against the cold inert gas in the boundary layer regions of the double heat pipe. To overcome this problem we have begun work on a new technique of metal vapor-metal vapor phase matching. In first experiments we have demonstrated a conversion efficiency of 4% in a mixture of sodium and magnesium vapor. The ratio of these metals for phase matching is about 1:0.8. Though conversion efficiencies have been impressive, the migration of magnesium limits run times to about one hour. A new type of heat pipe is contemplated to correct these difficulties.

During the year we have begun work on a new type of switched optical collision. In this process energy is stored in a metastable level of a first specie. To switch this stored energy to a radiating level of a second specie, tunable radiation of the correct frequency is incident on the system. Calculations show that in the presence of this radiation that the cross section for inelastic collisions between the two systems should be quite large. An experiment to demonstrate these ideas is now underway in a mixture of barium and calcium. If these experiments prove successful one of the major constraints to the operation of short wavelength lasers would be eliminated. To generate coherent radiation in the soft x-ray region, energy could be stored in the metastable level of some specie such as helium, and switched to, for instance, a selected excited ionic state.

Work also continues on a new type of broadband infrared to visible image up-converter. In this type of process two photons of an incident pumping laser are chosen such that the sum of the frequencies equals that of a non-allowed transition of an alkali metal vapor. The incident radiation sets up a symmetric fluctuation or vibration of the electron cloud. Low-level incident radiation connects this fluctuation to an allowed dipole transition, which then radiates. In recent experiments using two photons of a 1.079 μ laser as the pumping source, we have demonstrated 100% power conversion of an incident 3.1 μ source to blue radiation at 4600 Å. During the coming year we expect to use this device to form images in the infrared.

Several projects concerned with the construction of high power visible lasers are now beginning. These are based on various types of charge exchange collisions. In one system a mixture of calcium and strontium is used to store large populations in an excited metastable level of a strontium ion. An incident CO_2 laser will then be used to remove this stored energy via an anti-Stokes process. We believe that this is a very promising approach to the problem of obtaining high energy visible lasers.

A second system involves charge exchange collisions between zinc ions and calcium to yield output radiation at 3935 Å. Tunable ultraviolet radiation that we have developed during the past year is uniquely suited to study the charge exchange cross sections in this system. Based on initial theoretical work, we believe that the charge exchange cross section with the resonance line of the calcium ion should be quite large. If a vacuum ultraviolet diagnostics on this system proves successful, attempts at electrical excitation will begin.

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26. PSEUDOPOTENTIAL METHODS IN PHYSICS

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S. T. Pantelides

Graduate Students:

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D. Pettibone
R. Sokel

Agency Support:
NSF GP 39811
NSF through CMR
Army DA24

Technical Objectives:

To apply the pseudopotential approach to the microscopic theory of solids and molecules.

Research Report:

During this year we have essentially completed our formulation of the electronic structure of simple tetrahedral solids and the calculation of properties in terms of it. This has included studies of the piezo-electric and vibrational properties, and a complete study of the energy-band structure. The energy bands of these systems are of course well known and the achievement there was not so much in elucidating the band structure as in extracting very important information from it. We found in particular that a very good account of the energy bands could be achieved simply by adding three interatomic matrix elements to the single intra-atomic matrix element that was included in the initial Bond Orbital Model. We were from these able to deduce values for all of the nearest-neighbor matrix elements between atomic s- and p-states. These have proved essential in extending the approach to nontetrahedral structure such as graphite and semiconductor surfaces. We have at the same time completed the description of bonding properties of these systems by extending the Gordon-Kim interaction between closed-shell systems to the open-shell simple tetrahedral solids. This last piece was carried out by R. Sokel.

The study of semiconductor surfaces in terms of this approach has been particularly rewarding. We have been able to calculate the change in energy as the surface atoms are rearranged and discovered that the distortions should be very much larger than has been previously suspected. Using this approach we carried out a complete study of the reconstruction on the three principal symmetry surfaces of homopolar and heteropolar semiconductors, and the effect of atomic adsorption at the surface on each of these reconstructions. This has given the first complete picture of the surfaces and surface states. So little direct experimental information on these surfaces is available that it will be some time before the details of these extensive predictions can be tested.

At the same time S. Pantelides has continued his study of ionic solids, finding in particular that the traditional - and apparently universal - understanding of dielectric properties as the superposition of ionic contributions has been quite inappropriate; has provided an alternative understanding which is very much more accurate and convincing, without being appreciably more complicated.

Pantelides and I have also worked extensively toward an understanding of mixed tetrahedral solids, with SiO_2 being the central material. This first major extension of the Bond Orbital Model has been slow and difficult, but appears to be near completion, providing clear representations of the bonding properties as well as electronic structure.

I have also begun during the year an organization of all of this material, along with descriptions of bonding properties of metals, into a comprehensive solid-state chemistry text. I have built a course around that subject during the past year and the text is an integral part.

We hope during the coming year to complete the treatment of mixed tetrahedral solid and to expand into transition-metal oxides. However, the extraordinary advance this year has reached somewhat beyond our financial means and I anticipate therefore proceeding on a considerably smaller scale.

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27. FRACTURE OF COMPACT BONE

W. C. Hayes, Assistant Professor, Applied Mechanics and Surgery (Orthopaedics)

Professional Associates:

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D. J. Schurman

Graduate Students:

D. R. Carter
T. M. Wright
L. W. Swenson

Agency Support:

NSF through CMR
NIH 1 R01 AM 18376-01

Technical Objectives:

To characterize fracture processes induced by dynamic and cyclic loads in specimens of human bone and to correlate these processes with bone microstructure.

Research Report:

(1) Fatigue Properties of Compact Bone

Graduate Student: D. R. Carter

Fatigue tests to failure of compact adult bovine specimens were conducted at five stress amplitudes (65 to 108 MN/m^2) and four temperature levels (21 to 45^oC). Using photomicrographs, the specimens were categorized into four microstructure groups based on the extent of secondary Haversian remodeling. An analysis of covariance with multiple covariants was used to derive equations (corresponding to the microstructure groups) for fatigue life as a function of stress amplitude, temperature and bone density.

A significant positive correlation ($P < .01$) between fatigue life and bone density was shown within each microstructure group. In addition, a significant negative correlation ($P < .001$) was shown between density and the extent of Haversian remodeling. These data suggest that Haversian remodeling results in a reduced fatigue life not only by producing a less dense structure but also by creating an inherently weaker structure.

(2) Fatigue Crack Propagation in Bone

Graduate Student: T. M. Wright

Fatigue tests have been conducted on additional double cantilever beam specimens (DCB) machined longitudinally from the mid-diaphysis of fresh, adult bovine femora and tibia. The DCB specimens were 2.3 cm wide by approximately 7.6 cm long. Thickness ranged from 0.32 to 0.41 cm. Specimens were machined in a wet condition, equilibrated in Ringer's solution and stored at $-20^{\circ}C$ until testing. Microstructure studies of the fractured specimens were also performed by cutting away small cross-sections of bone near the fracture surface. The data collected from each specimen was plotted as crack length versus the accompanying number of cycles of loading and the corresponding value of the stress intensity factor was calculated from the boundary collocation expression of Gross and Srawley.

Fatigue crack propagation rates between 7.2×10^{-7} m/cycle and 3.4×10^{-4} m/cycle were measured for the bovine compact bone specimens. A strong correlation was found between the fatigue crack propagation rate and the range of stress intensity at the crack tip. Crack propagation was shown to occur by initiation and growth of subcritical flaws ahead of the main crack. The main crack propagated by joining with these flaws.

(3) Post-yield Behavior of Subchondral Trabecular Bone

Graduate Students: D. R. Carter and L. W. Swenson

Cylindrical specimens of bovine subchondral trabecular bone were tested to uniaxial compressive strain levels of 75 per cent to study energy absorption during pore collapse. Stress-strain curves were characterized by macroscopic yield at about 8 per cent strain followed by a significant horizontal pore collapse regime. Energy absorption occurred largely in this post-yield regime. Yield strength and energy absorption capacity were found to increase linearly with specimen apparent density. Microstructural analysis of the deformed specimens verified that the mechanism for energy absorption was primarily fracture and buckling of trabeculae. The results suggest that during fracture the collapse of trabecular bone (and the consequent absorption of energy) serves to attenuate stresses transmitted through the skeleton and thus protect vital structures such as the brain.

The Finite Element Method was also used to analyze stresses in the tibial condyles of a normal knee. Joint geometry was determined from a frontal section of the proximal tibia of a 22 year old male autopsy specimen with no previous history of joint disease. The three-dimensional, axisymmetric finite element model used 434 elements to account for the anatomic structure and material properties of the compact bone of the diaphysis, the cortical shell of the metaphysis and subchondral plate, two regions of cancellous bone, and a layer of articular cartilage. The models were loaded to 445 Newtons (100 pounds) distributed over 4.0 cm^2 on each tibial plateau. Under these loading conditions, the normal knee joint model predicted maximum compressive stresses in the subchondral bone of -2.17 MN/m^2. Regions of peak normal and shear stress were found to correspond closely to the common initiation sites for clinical fractures of the tibial plateau.

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12. Wright, T. M. and W. C. Hayes, "The Fracture Mechanics of Fatigue Crack Propagation in Compact Bone", Submitted April 15, 1975, J. Biomed. Materials Research.

28. MECHANICAL BEHAVIOR OF COMPOSITES UNDER IMPACT

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Graduate Students:
Terry Delph

Agency Support:
AFOSR
NSF through CMR

Technical Objectives:

As is generally recognized, two-phase composite materials, such as fiber-reinforced or layered solids, possess several features, which make them more attractive for certain technological applications than conventional macro-homogeneous materials. Thus the need arises to construct appropriate mathematical models to be used in describing analytically the mechanical behavior of such materials. It is the purpose of this program to develop suitable models and draw analogies to crystal lattice dynamics and the motions of electrons.

Approach:

In order to construct approximate theories, it is required to study in full detail the exact frequency spectrum of a layered composite which was never done before. The states of plane strain and anti-plane strain are studied in particular and the Fermi surfaces derived for these cases will be used as a guide in constructing approximate models.

Research Support:

(1) A Note on Critical Reflections of Waves in an Isotropic Elastic Plate

by R. K. Kaul and G. Herrmann

At grazing incidence of a flexural P-wave, or at grazing incidence of an extensional SV-wave, the wave motion vanishes in the case of an isotropic, elastic plate with traction-free surfaces. It is shown that by using d'Alembert's limiting procedure, the wave motion in these critical cases can be obtained from the Rayleigh-Lamb solution in a straight forward manner.

(2) Torsional Vibrations of a Hollow Cylinder with Periodic Structure

by R. K. Kaul and G. Herrmann

The theory of torsional vibrations of hollow cylinder, with a periodic structure of elastic constants and density variation normal to the axis of the cylinder is developed in terms of Floquet waves. Floquet waves are quasi-periodic, whose amplitude profile has the same periodicity as that of the material and thus repeats after traveling a complete cell of the cylinder. Using Floquet theory, the dispersion spectrum is obtained for time-harmonic waves propagating normal to the laminations. It is shown that the dispersion spectrum has a banded structure, consisting of passing bands and stopping bands. Some special cases, in which the wave profiles have simple forms are also considered. Also included in the analysis is the study of the mode shapes at the two ends of the zone.

(3) Torsional Vibrations of an Infinite Cylinder with Laminated Periodic Structure

by R. K. Kaul and G. Herrmann

The title problem has been carried out to completion, having had a two-fold purpose. First there exists a possibility that the frequency spectrum described free-harmonic vibrations of the composite cylinder might be such as to be potentially useful as a device in microwave technology. Indeed, torsional motions are being used in filter circuits and delay lines and the system to be studied which does not appear to have been investigated here-to-fore might offer improvements. Secondly, a number of efforts have been undertaken in recent years to construct a variety of approximate continuum theories to describe the dynamic behavior of composites. The availability of an exact solution of a problem based on the theory of elasticity for a bounded body will be most useful in assessing the merits of the various approximate theories which had been proposed.

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2. J. D. Colton and G. Herrmann, "Dynamic Fracture Process in Beams", ASME Paper No. 75-APMW-50, to appear in a forthcoming issue of the Journal of Applied Mechanics.

3. L. B. Freund and G. Herrmann, "Dynamic Fracture of a Beam or Plate in Plane Bending", submitted for publication in the Journal of Applied Mechanics.

4. Aynur Unal and George Herrmann, "On the Effect of Bonding in a Laminated Composite", SUDAM No. 75-2, Department of Applied Mechanics, Stanford University.

5. W. R. Delameter and G. Herrmann, "Weakening of Elastic Solids by Doubly-Periodic Arrays of Cracks", in Topics of Applied Continuum Mechanics, ed. J. L. Zeman and F. Ziegler, Springer-Verlag 1974, pp 156-173.

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29. STRUCTURAL STUDIES OF PROTEINS

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Graduate Students:

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T. K. Eccles
J. Phillips

Agency Support

NIH CA 16748
PRF 2887-G3
Research Corporation
NSF through SSRP

Technical Objective:

Investigation of the structures of biomacromolecules on a molecular level.

Approach:

Two approaches are being used. We are applying conventional X-ray diffraction methods to investigate the crystal structures of three proteins, nerve-growth-factor, monellin and L-glutaminase-asparaginase. In addition, unconventional synchrotron radiation is being exploited as a source for X-ray diffraction studies as it offers high intensity and tunability. The second approach being used is that of extended X-ray absorption fine structure spectroscopy (EXAFS) to investigate the local geometry around the metal centers in metalloenzymes. Information about the oxidation state and coordination site geometries in proteins such as nitrogenase, hemoglobin and hemocyanin is being obtained.

Research Report:

(1) X-ray Diffraction Studies of Proteins Using Conventional and Synchrotron Radiation

Postdoctoral Fellows: A. Wlodawer
M. Yevitz

Graduate Students: J. Phillips

The three-dimensional structures of several proteins which play regulatory roles in the growth of normal and tumor cells are being investigated. These proteins are (1) nerve-growth-factor (NGF), a small protein (MW 26,500) isolated from mouse submaxillary glands, which enhances growth and development of sympathetic and embryonic sensory nerve cells; (2) L-glutaminase-asparaginase (GLA) from Acinetobacter, an antitumor protein containing four subunits (MW 33,000 each); and (3) neocarzinostatin (NCS), an antitumor protein isolated from Streptomyces carzinostaticus. NCS has been crystallized and preliminary studies of the crystals begun. Crystals of NGF have been grown by vapor diffusion from ethanol solution. The crystals are hexagonal with space group $P6_122$ with a=56.1 Å, c=181.4 Å, and V=494,400 $Å^3$. Several heavy atom derivatives have been prepared by soaking the crystals in solutions containing heavy metal ions (lanthanides, platinum, palladium, and mersalyl) and preliminary investigations suggest that they are isomorphous. Two crystal forms of GLA have been grown by vapor diffusion of 40% 2-methyl-2,4-pentanediol into protein solution and the crystals have been studied by X-ray diffraction and electron microscopy. Form I crystals are hexagonal, $P6_2$ with a=145.0 Å, c=63.5 Å. Form II crystals belong to the orthorhombic space group $C222_1$ a=149.7, b=70.5 and c=132.8 Å. Studies of the structure of all three proteins is continuing using X-ray diffraction and electron microscopy techniques. Crystal diffraction is also being studied using synchrotron radiation. Because of the very high intensity and tunability of this unconventional source, the use of anomalous scattering techniques will be much facilitated. This source has been used to collect anomalous projection data on the protein rubredoxin.

(2) Extended X-ray Absorption Fine Structure Spectroscopy

Graduate Students: S. P. Cramer
T. K. Eccles

X-ray absorption spectra are characterized by several sharp edges of rapidly increasing absorption coefficient μ. Closer examiantion of the high energy side of the edges reveals periodic damped oscillations in μ; this Extended X-ray Absorption Fine Structure has been called EXAFS. Using the Stanford electron storage ring SPEAR as an X-ray source, we are developing EXAFS Spectroscopy as a tool for the study of metalloproteins. Two systems have been chosen for preliminary studies: hemoglobin and the Mo-Fe component of nitrogenase. For hemoglobin, a series of Fe(II) and Fe(III) tetraphenylporphyrins, with and without axial ligands, has been studied by EXAFS. The spectra are sensitive to both the oxidation state of iron and to the presence of axial ligands. J. P. Collman's "picket fence" hemoglobin model has been examined with and without bound oxygen, to observe the effect of oxygen binding on the Fe-porphyrin geometry. Finally, EXAFS spectra for oxy- and deoxy-hemoglobin have been taken, in an effort to test the "trigger-mechanism" model for hemoglobin cooperativity. The Mo-Fe component of nitrogenase has also been examined by EXAFS spectroscopy. The spectrum is being compared with a series of molybdenum compounds of known oxidation state and Mo-Mo distances, in order to gain the same information about the metal environment in nitrogenase.

Reference Publications:

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30. PHYSICAL STUDIES OF MOLECULES OF BIOLOGICAL INTEREST

B. S. Hudson, Assistant Professor, Chemistry

Graduate Students:

J. R. Andrews
S. P. Cramer
J. H. Dawson
J. J. Diamond

W. M. Hetherington
R. E. Jacobs
H. A. Karp
L. A. Sklar

Agency Support:

Alfred P. Sloan Foundation
Camille and Henry Dreyfus Foundation
American Cancer Society

NIH CA 15461
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NIH EY 01518

Technical Objectives:

To develop new methods for the study of large organic molecules and biomolecules especially using electronic and vibrational spectroscopy. Current interest centers on fluorescence, Raman and inelastic neutron scattering techniques and non-linear Raman spectroscopy. Theoretical procedures are used in the design and analysis of experiments.

Approach:

Electronic energy levels of large conjugated organic molecules are studied by investigation of mixed crystal (solid solution) samples near the absolute zero of temperature. The vibrational motions of large molecules are studied by Raman and inelastic neutron scattering techniques coupled to consistent force field conformational and normal mode calculations. Buoyant density ultracentrifugation methods are used in conjunction with room temperature fluorescence in the study of closed circular DNA. Resonance Raman methods are used to study both electronic and vibrational levels in conjugated molecules. Linear conjugated polyenes are used as fluorescence and Raman probes of membrane structure. A new non-linear Raman technique known as coherent anti-Stokes Raman scattering is being developed.

Research Report:

(1) The Electronic Spectroscopy of Linear Polyenes
(see reference 1)

Graduate Students: J. J. Diamond
W. M. Hetherington

Linear polyenes are conjugated chains of alternating double and single carbon-carbon bonds. Their electronic spectroscopy is of interest from the biological point of view because the visual pigments contain a linear polyene as the photoactive unit. These molecules are also of interest from a theoretical point of view because they are apparently inadequately described by most simple molecular orbital theories. It has recently been shown that the lowest energy excited singlet state of all linear polyenes consists of a mixture of singly and doubly excited configurations in the molecular orbital picture or to an exciton state derived from two ethylene triplet excitations (see reference 1). Resonance Raman experiments have confirmed the assignment of the vibrational intervals observed in the high resolution mixed crystal spectra of the polyene diphenyloctatetraene. A method has been found for the synthesis of linear polyenes which are part of a long saturated fatty acid chain. Mixed crystals of these polyenes, β-carotene, stilbene and other molecules of interest have been prepared. The implications of this revised state ordering for the photochemistry of polyenes is also being investigated. Two-photon spectral studies of linear polyenes are in progress. Recent progress in the synthesis of very long chain polymeric polyenes (polydiacetylenes) has opened up a new interest in polyenes as materials.

(2) Improved Dye-Buoyant Density Procedure for the Isolation of Closed Circular DNA

Graduate Student: J. Dawson

Many organisms (including man) contain DNA in which both of the phosphodiester backbone chains are in the form of covalent circles. These molecules are of great medical interest because of their presence in animal tumor viruses and the occurrence of unusual closed circular forms in leukemia patients. A very efficient procedure for the preparation of closed circular DNA involves the interaction of the dye ethidium bromide with DNA in a buoyant density gradient. The buoyant density mixture consists of water, ethidium bromide, cesium chloride and the DNA of interest. At equilibrium, there is a separation between closed circular DNA and linear DNA or circular molecules which have suffered at least one backbone strand scission. The DNA bands are easily detected because of the enhanced fluorescence of the ethidium cation when it is bound to DNA. We hope to improve the resolution of this technique by modification of the ethidium nucleus or the use of inorganic salts other than cesium chloride. Previous results indicate that increasing the mass of the ethidium cation by appropriate substitution will increase the resolution by as much as five fold. A modification of this procedure has been devised such that the fluorescence detection sensitivity of the DNA bands is so large that it is competitive with radioactive tracer methods.

(3) The Electronic Spectroscopy of Ethidium Bromide

Graduate Student: R. Jacobs

Ethidium bromide is a complex heterocyclic molecule used in the dye-buoyant density procedure described above. Ethidium has a very poor fluorescence quantum yield in water. When the molecule binds to DNA, its fluorescence is enhanced by about 25 fold. This fluorescence enhancement is the basis for a very useful detection method for DNA species. For this reason, and because of its intrinsic interest, we would like to understand the mechanism for the fluorescence enhancement of ethidium. The problem is made even more interesting by the fact that other molecules with structures similar to ethidium which bind to DNA by the same mechanism show a decrease in fluorescence on binding. The fluorescence enhancement for ethidium is due to a change in the radiationless decay rate for the lowest energy excited singlet state. We have obtained preliminary evidence that the decay of this state occurs primarily by intersystem crossing to a triplet level which is nearly degenerate with the lowest singlet. The singlet level shifts below this triplet on binding to DNA and thus the decay channel is closed. Magnetic circular dichroism and low temperature absorption studies of ethidium have greatly increased our knowledge of the excited singlet levels. This knowledge will be used in conjunction with phosphorescence and triplet-triplet absorption experiments to determine the energies of the triplet levels. It has been found that ethidium has a greater fluorescence efficiency in deuterium oxide than in normal water by a factor of about 3 and that it has a much lower fluorescence efficiency in concentrated iodide salt solutions than in concentrated chloride solutions. This last effect will be used to enhance the detection efficiency of the dye-buoyant density procedure.

(4) Studies of Membrane Structure and Dynamics by Raman and Fluorescence Methods

Graduate Students: L. A. Sklar
J. R. Andrews

The structure and properties of phospholipid bilayers is a subject of great current interest because of the relevance of these studies to an understanding of the function of biological membranes. We propose to study these structures by a combination of Raman, resonance Raman and fluorescence label techniques. The Raman studies are based on the fact that the normal modes of the hydrocarbon side chains of phospholipids are sensitive to the conformation of the chain. An analysis of the observed spectra using the normal coordinate analysis methods described below will yield information on the conformational changes of the phospholipids. Measurements of the degree of polarization of the Raman lines should yield information on the spatial distribution of the various conformational species. Fatty acids containing conjugated polyene chains have been synthesized and incorporated into phospholipid bilayers. These probe molecules can be observed by resonance enhanced Raman spectroscopy and fluorescence. They will accept energy from excited aromatic amino acids so that energy transfer experiments are possible. The fluorescence intensity of the polyene probes is very sensitive to the phase transition behavior of model membrane systems and we expect that it will also be sensitive to the trans-membrane electric field. These polyene probes are biologically incorporated into membranes by living organisms and can be detected with very high sensitivity (10^{-8} molar).

(5) Consistent Force Field Calculations and Inelastic Neutron Scattering Spectroscopy (see references 2 and 3)

Graduate Student: H. A. Karp

Inelastic neutron scattering spectroscopy can be used as a technique for molecular vibration spectroscopy similar to Raman scattering. Neutron scattering differs from optical methods in that many low frequency normal modes which are very weak or absent in IR and Raman spectra are strong in the neutron scattering spectra. Neutron scattering is interesting from the theoretical point of view because the intensities of inelastic events can be calculated from an assumed knowledge of the nuclear vibrational motion. This is in contrast to the calculation of IR and Raman intensities where a knowledge of dipole and polarizability changes must be available. The information needed for a neutron scattering calculation consists of the vibrational normal mode eigenvalues and eigenvectors which can be obtained from a reliable normal mode calculation. We have used the consistent force field potential of Lifson and Warshel to calculate neutron scattering spectra of saturated hydrocarbons. The parameters for the force field were taken from Lifson and Warshel who had adapted them to fit conformational, vibrational and thermodynamic data. The agreement between calculated and observed inelastic neutron scattering spectra was very good. Experimental work is under way involving neutron scattering spectra of molecular crystals and model membrane systems.

(6) Coherent Anti-Stokes Raman Scattering (see reference 4)

Graduate Student: S. P. Cramer

Coherent anti-Stokes Raman scattering (CARS) is an exciting new technique for obtaining Raman spectra with very high signal levels and high signal to noise ratios. The technique involves a non-linear mixing process which results in a very high conversion of incident power to signal when two high peak power pulses with different frequencies are crossed in a sample. A high signal to noise ratio occurs because the signal is produced as a coherent beam and because no monochrometer is needed (the spectrum is scanned by varying the frequency difference between the two incident beams). This technique can be used to strongly discriminate against fluorescence because of the low spatial divergence of the signal beam and because of the anti-Stokes frequency.

This technique is ideally suited to studies of dilute biological systems containing chromophores by resonance enhanced CARS scattering. One of the many advantages of CARS is that low average power levels are used which minimizes sample damage. A particularly exciting application of CARS involves the detection of vibrational optical activity via circular intensity differential Raman scattering.

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2. Bruce S. Hudson, Arieh Warshel and Roy G. Gordon, "Inelastic Neutron Scattering: Computational Methods Using Consistent Force Fields," J. Chem. Phys. 61, 2929 (1974).
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31. SOLID STATE ELECTROCHEMISTRY

R. A. Huggins, Professor, Materials Science and Engineering

Professional Associates:

- B. Boukamp
- A. G. Elliot
- N. Endow
- L. E. Nagel
- I. D. Raistrick
- J. Schoonman

Graduate Students:

- O. B. Ajayi
- U. Cohen
- L. B. Ebert*
- M. T. Gur
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- C. Ho
- C.-H. Hsieh
- Y. W. Hu
- S. Lewkowitz**
- B. E. Liebert
- A. R. Yavari

*Received PhD during report period.
**Received MS during report period.

Agency Support:

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ARPA through CMR

Technical Objectives:

(1) Development of new materials for use in high performance battery and fuel cell systems. This involves design, synthesis and characterization of new inorganic materials as well as evaluation of their thermodynamic and transport properties.

(2) Applications of solid state electrochemical techniques for scientific and engineering studies. This includes work on catalyst materials, electrocrystallization, selective ion sensors, etc.

Research Report:

(1) Mass and Charge Transport in Fast Ion Conductors

Theoretical models are being developed and experimental measurements made of the defect structure, and ionic and electronic conductivity in several groups of solids with highly mobile ionic species. Particular attention is being devoted to materials with crystal structures containing tunnels and sparsely populated layers. These include beta alumina, alkali metal ferrocyanides, titanates, germanates, silicates, alumino silicates, fluorides and related materials.

Experimental methods being utilized include nuclear magnetic resonance and ionic conductivity measurements, as well as several techniques for the evaluation of time-dependent transport in solid state electrochemical systems. The latter include dielectric loss, thermal depolarization, complex admittance, and potentiostatic experiments.

(2) Use of Solid State Electrochemical Techniques to Control Catalysis

Elevated temperature solid state electrochemical cell techniques are being developed and used to characterize and control the defect structure and properties of ionic conductors and mixed conductors, with particular reference to their catalytic properties. Primary effort is now directed at studies of the catalytic decomposition of nitric oxide, a common constituent of exhaust gases.

(3) Synthesis and Structure of Materials with Intercalated Layer Structures

Several techniques are being used to synthesize and study groups of materials with intercalated layer structures. Present work involves graphite compounds, some of which appear to be particularly interesting as battery components, and as possible catalysts.

(4) Exploration of a New Method for the Synthesis of Oxides

A new method, involving the controlled decomposition of polymeric precursors, is being explored for the synthesis of oxides and other compounds. Current work is aimed at the preparation of beta alumina, an important solid electrolyte.

(5) Novel Solid State Battery and Fuel Cell Systems

Several new concepts for the development of high performance batteries and fuel cells based upon the use of solid electrolytes are being explored. Particularly interesting are systems with high values of energy density utilizing mixed conducting solids as electrode components.

(6) Development of Electrochemical Techniques for Crystal Growth

Both theoretical and experimental work are underway on the use of electrochemical techniques for the growth of both single crystals and polycrystals. Of particular interest at the present time is electrocrystallization of intermetallic and metal-metalloid compounds from molten salt systems. Materials being studied include niobium superconducting compounds, sulfides, phosphides, hexaborides, and materials with the tungsten bronze and related structures.

Reference Publications:

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2. T. K. Halstead, "Proton NMR Studies of Lanthanum Nickel Hydride: Structure and Diffusion," Jour. Solid State Chem. 11, 114 (1974).
3. R. A. Huggins, "Ionic Conduction in Oxides at Low Temperatures," in Defects and Transport in Oxides, edited by M. S. Seltzer and R. I. Jaffee, Plenum Pub. Corp., New York (1974), pp. 549-566.
4. L. B. Ebert, R. A. Huggins and J. I. Brauman, "Wide Line Nuclear Magnetic Resonance of ^{19}F in Graphite-Antimony Pentafluoride: Evidence for Rapid Motion of Intercalated Species," J.C.S. Chem. Comm., 924 (1974).
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32. STUDIES IN PHYSICAL PROCESS IN GEOLOGY

Arvid M. Johnson, Associate Professor, Geology and
Applied Earth Sciences

Graduate Students:

A. Aydin
J. A. Baltierra
S. M. Eston
J. H. Fink
C. E. Hill
C. R. Holzhausen
E. G. Honea
Z. Reches
J. Rodine*
D. Scofield
A. E. Soto**
J. Trummel**
D. Hoexter**
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R. W. Turnbull
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*Received PhD during report period.
**Received MS during report period.

Agency Support:

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Penrose Fund, Geological Society of America
Engineering Geology Branch, U. S. Geological Survey

(A) FOLDING AND FLEXURING OF MULTILAYERED ELASTIC AND VISCOUS MATERIALS

Graduate Students: J. H. Fink, C. E. Hill, E. G. Honea, Z. Reches, D. Scofield

Technical Objective:

To understand why rocks typically fold into concentric, chevron and kink forms, to explain small folds in silicic lavas, and to explain how monoclinal flexures might form.

Approach:

Theoretical, field and experimental studies of folds and processes of folding. Theories of nonlinear elastic and viscous materials and of characteristics. Experiments primarily with multilayers of photoelastic rubber and gelatin. Field studies near Flagstaff, Arizona, and near Glass Mountain, Santa Maria, Darwin, and Oroville, California.

Research Report:

Sinusoidal, concentric and chevron folds in elastic multilayers apparently form sequentially so that sinusoidal folding establishes a wavelength, concentric folding modifies the wavelength as a function of position in the gross fold pattern and chevron folding results from migration of cores of concentric forms into a multilayer. Kink folds appear to be fundamentally different, developing in layers that have frictional contacts which slip when sufficient shear develops. Thus, kink folding appears to be a type of failure, akin to faulting.

(B) SETTLING OF SAND IN HOMOGENEOUSLY TURBULENT WATER

Graduate Student: J. Baltierra

Technical Objectives:

To determine effects of ambient turbulence in water on settling velocities of spherical particles.

Approach:

Theoretical and experimental analyses of relative movements of water and a dense sphere under conditions approaching homogeneous turbulence. Sedimentologists use relative settling velocities of heavy and light mineral grains in sedimentary rocks to distinguish among various environments of deposition. Settling velocities are determined in still water whereas water in most natural environments of deposition is turbulent. The primary purpose of the research is to evaluate effects of turbulence of this method of estimating depositional environments.

(C) MOBILIZATION OF DEBRIS FLOWS

Graduate Student: J. Rodine

Technical Objective:

To learn to predict where debris flows or mudflows are likely to occur.

Approach:

Theoretical analysis of plastic behavior of granular solids in various situations. Theoretical analysis of packing of particles of various sizes. Experimental measurements of size distributions and strength properties of natural debris and of effects of size. Distributions of spherical particles on debris strength. Field mapping of source areas of natural debris flows in the Sacramento Valley, near Los Angeles, and at Big Sur.

Research Report:

Strength of artificial debris can be understood quite well in terms of interlocking friction amongst coarse grains and of cohesive strength of a fluid phase of water and clay. By means of a packing model based on tetrahedral units of four spheres of unequal diameters, the concentration of spheres required to interlock the spheres can be calculated. Theoretically, if the spheres are loosely packed, the debris should be quite mobile. The packing model has been applied to size analyses of a wide range of natural materials. The model can readily distinguish between many natural materials such as beach sand and debris-flow material and the sorting coefficients of the materials appear to be useful indicators of the potential for debris flow of the materials.

(D) ORIGIN OF SHEET STRUCTURE IN GRANITE

Graduate Student: G. Holzhausen

Technical Objective:

To understand how sheet structure develops in granitic rocks.

Approach:

Field observation of sheet structure in a granite quarrry in

New England, measurement of stresses in quarry rock, experimental and theoretical analyses of development of large sheet fractures.

(E) MECHANISMS OF FAULTING IN SANDSTONE AND SHALE

Graduate Student: A. Aydin

Technical Objective:

To develop a theory to explain patterns of shear in sedimentary rocks along and near small normal faults in the Henry Mountains area.

Approach:

Field observation and mapping of meso and micro structures in and near fault zones, thin-section analysis of deformation of the rocks, theoretical and experimental analysis of the development of the structures.

(F) MECHANISMS OF EARTH FLOW

Graduate Students: D. Keefer
R. Turnbull
D. Yadon

Technical Objective:

To determine why some landslides transform into tongues of soil that slowly flow down hillslopes and to learn to predict the critical conditions of such earth flows.

Approach:

Field mapping and measurement of movement rates and pore-water pressures of selected earth flows in the Bay Area. Theoretical analysis of large deformations of soils. Laboratory testing of strength and flow properties of samples from active and inactive earth flows and from sources of earth flows.

33. ACOUSTIC INTERACTIONS WITH SOLIDS

G. S. Kino, Professor, Electrical Engineering

Professional Associates:

J. F. Havlice
H. Hayakawa

Graduate Students:

H. R. Gautier
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B. T. Khuri-Yakub
R. Joly
S. Bose
P. G. Borden
J. D. Fraser

Agency Support:

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Navy N00014-67-A-0112-0084
Navy N00123-72-C-0866
AF F-30602-74-C-0038
AMROC RI 74-20773

Technical Objectives:

To develop monolithic acoustic surface wave convolver devices capable of taking the convolution or correlation between two arbitrary signals. These are to be used to store arbitrary signals, and to scan and take transforms of optical images.

Research Results:

We have been developing a monolithic ZnO on Si convolver in order to eliminate problems with the airgap in the more conventional Si on $LiNbO_3$ convolver. These convolvers have proved to be efficient, have shown optical sensitivity because the output is affected by the presence of light, and have been used to recognize digital codes. We have made convolvers with good uniformity and efficiency of P_{out}/P_{in1} P_{in} [illegible] 58 dbm. The ZnO deposition technique produces ZnO with an effective coupling coefficient $k_T = 0.25$, which compares with the theoretical single crystal value of $k_T = 0.28$. When the ZnO is deposited on Si there are problems with interface states between the ZnO and SiO_2. We are currently tackling these problems. There are also problems with surface states at the S_i-SiO_2 interface, due to the relatively high temperature used for the deposition of ZnO, and the difficulty of annealing after making the device.

At the present time we are working with buried channel type of devices in which a series of pn junctions are laid down in the Si, and the interaction takes place underneath the surface in the depletion layer of the pn junctions.

A thesis has been written on the acoustical scanning of optical images. Various types of real-time Fourier transforms and optical images of Fresnel transforms have been taken, and it has been demonstrated that the inverse transform can be taken to reconstruct the original optical image. The theory of these devices has been developed in some detail. It makes it possible to use the experimental measurements to measure the time constants of the surface state traps, the surface state density, and the distribution of trap density as a function of energy level. Thus, the acoustic techniques provide an important new method of measurement of semiconductor surfaces. In this case, no metal electrodes are required. All that is required is a piece of carefully oxidized Si, which is placed close to a $LiNbO_3$ piezoelectric substrate.

II. Acoustic Scanning of Optical Images.

Technical Objectives:

To use acoustic surface wave techniques to focus and scan on low frequency acoustic images. The applications are to non-destructive testing, medical imaging, and undersea imaging.

Research Results:

We have described in previous reports an acoustic imaging system in which acoustic surface wave techniques are used to scan and focus on an object illuminated by an acoustic beam in the 1-5 MHz range. We have constructed an 83 element piezoelectric array as a receiver which scans and focuses along a line in the x direction. By placing an object in the focal plane of the receiver and illuminating it with a slit source or an acoustic beam focused to a line with a cylindrical lens, we are able to scan the object electronically in the x direction and mechanically in the y direction. We have been working on an NDT application using a boron reinforced epoxy laminate laid down on titanium. We have been able to visualize the debonded regions in these samples with good accuracy. The great advantage of the technique is that, because electronic scanning is used, the scan time is reduced to a few seconds in a sample 9" x 3". This is a reduction of almost 100 in the time required for purely mechanical scanning in both directions.

A new system has also been developed in which the array is used both as a transmitter and receiver. This system is intended for reflection imaging of flaws in various kinds of material. At the present time it scans a raster approximately 5-20 cm in the z direction perpendicular to the array and 5 cm in the x direction parallel to the array. We have obtained a definition with this system of 2 in both directions. So far we have measured stepped metal samples and have obtained excellent reproduction of the steps.

Reference Publications:

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3. B. T. Khuri-Yakub and G. S. Kino, "A Monolithic Zinc-Oxide on Silicon Convolver", Appl. Phys. Lett., 25, 188-190, August, 1974.
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34. ANALYSIS OF METAL FORMING AND VISCOELASTICITY

E. H. Lee, Professor, Applied Mechanics

Professional Associates:

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S. Mukherjee
T. Wierzbicki

Graduate Students:

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G. A. Nystrom
R. W. Young
T. Wertheimer

Agency Support:

DOT OS-30091
ONR N00014-67-A-0112-0081, 0083
DAA-G46-74-C-0057

Technical Objective:

Develop improved and more general methods of stress and deformation analysis for metal forming. Particular emphasis is on steady state problems, such as extrusion and wire-drawing, which comprise the methods most commonly used. It is expected to be able to determine the limiting conditions for satisfactory operation before the onset of metal-forming defects.

Research has also been carried out on the thermodynamics of viscoelastic media. Temperature effects can have such a major influence on the response of polymers to loading, that thermo-viscoelastic analysis is needed for studies of the structural strength of such materials, particularly under impulsive loading.

Approach - Research Report:

(1) Finite Element Analysis

Graduate Students: K. A. Derbalian
T. Wertheimer

We have developed an elastic-plastic finite-element computer program to analyze deformation to finite strains. Elastic-plastic analysis is required in order to evaluate the stress distribution which is needed to assess forming conditions which will yield successful operation. So far we have studied the deformation of porous metals, to assess their facility to absorb energy in the plastic flow associated with pore collapse. We are now studying means of modifying the program to treat steady-state problems.

(2) Bounds on Deformation in Impact

Graduate Student: G. A. Nystrom

We have unified and extented theorems which give upper bounds and lower bounds which bracket the exact value of the final deformation of a ductile structure subject to impact. This work may provide a rapid means of analyzing dynamic plastic deformation.

(3) Thermo-Mechanical Effects in Polymers

Graduate Student: R. W. Young

The thermodynamics of polymers has been studied in order to determine the temperature change caused by loading. Both oscillatory and transient loads have been considered.

Reference Publications:

1. E. H. Lee, R. L. Mallett, T.C.T. Ting, and W. H. Yang, "Dynamic Analysis of Structural Deformation and Metal Forming", Comp. Meth. in Appl. Mech. and Eng. 5, 69-82, 1975.

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35. STRUCTURE OF DENSE FLUIDS

J.E. Lind Jr., Chemical Engineering

Graduate Students:

R.F. Cleverdon*
H.L. Lips
C.-L. Lu

*Received Ph.D. during report period

Agency Support:

NSF GK 38120
NSF through CMR

Technical Objective:

To relate the thermodynamic and transport properties of dense fluids to the structure of the fluid and in particular to understand the effects of long range coulomb fields as well as the strongly directional interactions of hydrogen bonds upon these properties. The effects of these interactions are being examined in three types of comparisons: (1) liquid metals compared to nonmetals; (2) liquids of dipolar molecules compared to nonpolar liquids; and (3) hydrogen bonded fluids compared to nonhydrogen bonded, polar fluids and nonpolar fluids.

Approach:

Each experimental system of a liquid with strong electrostatic forces or hydrogen bonding between molecules is chosen so that there is also a reference liquid system without these forces, yet with molecules essentially isoelectronic to those in the system with strong interactions. In this fashion the properties of the reference system can be subtracted from those of the liquid with strong intermolecular forces at the same temperature and volume. This difference can be used to test perturbation theories of the liquid state and/or to infer the magnitude of effects which theory cannot yet treat. These experimental perturbations are usually much less sensitive to the detailed structure of the molecules of the reference system, such as their nonsphericity, than are the properties of the reference system itself and so the reference system can be treated as a simple system such as a system of hard spheres.

A very precise technique for measuring PVT properties permits evaluation of the first and second order configurational derivatives of energy and entropy up to 8 kbars in order that volume and temperature can be easily varied by over 30%. Self diffusion measurements are made under pressure by spin-echo NMR and related to the thermodynamic properties.

Research Report:

(1) Liquids with Hydrogen Bonded and Dipolar Molecules.

Graduate Student: R. Cleverdon

a) The thermodynamic properties of the reference system of neopentane have been compared to those of the isoelectronic molecule trimethylamine borine, which has an offset dipole. Other nearly isoelectronic molecular liquids such as t-butyl chloride, fluoride, and cyanide were also investigated. The differences of the thermodynamic properties from those of the reference neopentane were then calculated using Stell's perturbation technique.

The compressibility factor and the bulk modulus were separated into their entropy and energy contributions. Both theory and experiment showed that the entropy contribution to both properties was not significantly effected by the dipolar interactions.

The offset dipoles were represented by multipole expansions and, for the small offsets in the amine borine, the theory was able to calculate 80% of the energy in this case where there is a large dipole of 4.6 Debye. However, the results were not nearly so good in the case of the cyanide where the dipole is smaller but the offset larger. The Stell method may be adequate but the Padé approximant must be formed for the quadrupole terms as has been done for the dipole. Thus the theory is adequate but higher multipoles are necessary.

b) To investigate hydrogen bonding, t-butyl alcohol and amine were compared to neopentane. The difference between the energy surfaces of the alcohol and neopentane was attributed to the hydrogen bonding. A simple theory suggested by H. C. Andersen in which the hydrogen bond was treated as a small square well was applied. In this theory each molecule could make up to two independent hydrogen bonds. The theory fitted at two temperatures along an isocore yielded the correct density dependence of the hydrogen bond energy and showed that hydrogen bonds tend to form in greater numbers as the density is isothermally increased. The hydrogen bond energy required to fit the theory was 5.65 kcal/mole which is in good agreement with energies estimated by other methods. Experimentally there was only a slight effect on the entropy contributions to the compressibility factor and bulk modulus in contrast to the theoretical prediction. This result suggests that the hydrogen bonds are not nearly so localized as the model suggests, but the energy is well represented by the model.

(2) Thermodynamics of Liquid Metals.

Graduate Student: C.-L. Lu

The immediate goal of this research is to provide thermodynamic data with which to test theoretical models of liquid metals. In additional to mercury, which was previously studied in this laboratory, gallium, sodium, potassium and rubidium have been studied. The data are of sufficient accuracy that both the compressibility factor and the bulk modulus can be separated into configurational derivatives of the entropy and energy. The data for the liquid alkali metals show conclusively that the bulk modulus depends only upon the energy of the coulomb interactions in contrast to nonmetals such as argon where it depends largely upon the entropy of packing molecules in the liquid. The pressure, bulk modulus and kinetic pressure coefficient have been calculated from a model using pseudopotentials to calculate the ion-electron interaction, and a coulomb repulsion with screening between ions. The structure factor was calculated from the effective potential using a perturbed hard sphere model as suggested by Andersen. Agreement for this one parameter model was generally excellent except for mercury where an ion-ion core repulsion was required in order to fit the kinetic pressure coefficient. This data and the application of theory to it are the first to show how accurately this simple perturbation technique is for calculating the volume and temperature derivatives of the structure factor. The importance of these results is that the entropy and energy contributions to thermodynamic properties are separated out experimentally and provide constraints to determine the adequacy of the model.

(3) Self-diffusion in Liquids.

Graduate Student: H. Lips

Self-diffusion measurements as a function of pressure and temperature were made by spin-echo NMR with a fixed field gradient. Measurements on neopentane were compared to those on t-butyl alcohol. At the same volume and temperature, the alcohol self diffusion coefficients were only about 30% below those of neopentane. As suggested above by the small entropy effects of hydrogen bonding, the hydrogen bonds have only a small effect upon the diffusion.

Next, self diffusion was related to thermodynamic properties. First a relation has been derived between thermodynamic properties and the second space moment of the Laplacian of the pair potential. Experimental thermodynamic data show this Laplacian as primarily determined by the configurational derivatives of the entropy. The Laplacian itself is proportional to the second moment of the frequency spectrum of the velocity autocorrelation function and in general this moment shifts slightly more slowly to higher frequency with increasing density than the self diffusion coefficient decreases. Models are being developed to relate these properties.

An extremely simple model has been shown to be applicable to calculate the diffusion coefficient of neopentane within 20%. The kinetic pressure coefficient is fitted by the hard sphere theory for the fluid state and the resulting hardsphere diameter is used in the Chapman-Enskog theory for diffusion which is then corrected by Alders empirical correction from molecular dynamics. While the calculated results are 20% high at any temperature the density dependence is given correctly. Such an approach should be very useful for engineering estimates of self-diffusion coefficients.

Reference Publications:

1. R.F. Cleverdon, "Configurational Thermodynamic Properties of Polar and Hydrogen Bonding Liquids," Ph.D. Thesis, Stanford University, Stanford, CA, May 1975.

36. SUPERCONDUCTIVITY AND MOLECULAR PHYSICS

W. A. Little, Professor of Physics

Professional Associates:

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Agency Support:

NSF through CMR
NSF GH 41213
NASA JPL 953752
NASA NGL 05-020-242
Research Corp.

Technical Objective:

To study the feasibility of obtaining superconductivity at a relatively high temperatures in organic and organo-metallic systems. To develop means for detecting the presence of molecules by structure specific sensing techniques. To understand how information may be imprinted and recalled in a neural network.

Approach:

Our main line of work is the study of the possibility of high temperature superconductivity using an exciton induced electron-electron interaction rather than the phonon mechanism. Our efforts have centered on linear chain systems where we believe a sufficiently strong excitonic interaction can be obtained with suitable ligands. We have developed a new class of dye complexes based on a planar phenanthroline ligand structure. Several simple examples of this class have been prepared similar to the classic Magnus Green Salt structure. Numerical calculations of a possible superconducting transition temperature T_c in certain of these give promise of achieving superconductivity at relatively high temperatures.(1) Effects of the lattice stability, renormalization of exciton energies and fluctuations effects are now being considered. A preliminary result shows that the nature of the exciton interaction is to cause it to favor superconductivity over the Peierls insulation state. This theoretical result is being checked numerically for certain special systems.

Experiments have been done to determine the conductivity of various samples by d.c., a.c. and optical means. Using our He^3 - He^4 dilution refrigerator in collaboration with R. L. Greene and G. B. Street of IBM, San Jose, we observed superconductivity in the polymeric solid $(SN)_x$ at 0.26°K.(2) This important result establishes the fact that the superconducting state can be obtained in a polymer. Measurements on other purely organic system of the TTF-TCNQ type have shown certain of these to remain metallic down to 0.045°K, our present limit of measurement. Other polymeric systems are currently being developed.

A new extremely sensitive immunoassay technique for the detection of specific types of molecules by fluorescent tagging has been developed.(3) The technique relies on the selective binding of the appropriate antibody onto a glass surface to which antigen has been adsorbed. Then antibody labeled with fluorescein dye is added to the test solution, the antigen in solution must compete with the antigen on the surface for the antibody. Using a total internal reflectance technique the evanescent wave is used to excite the fluorescence of molecules bound to the surface but not those in solution. The intensity of the fluorescence light is then a measure of the concentration of free antigen in solution. A patent on this device has been filed and our claims accepted. A multiple assay device is now being developed. We have continued work on our analogy between the time evolution of the states in a neural network such as the brain and a two-dimensional Ising model.(4) It has been shown that a correspondence exists between the long range order in a spin system and short term memory in the brain. This model has been extended to explain learning, short and long term memory and the process of recall.(5) The holographic nature of the information storage in the model has been explicitly demonstrated. A microminiature hardware device has been designed to simulate the behaviour of the neuron as predicted by our model. Several prototype models have been built in collaboration with personnel from the Intergrated Circuit Laboratory.

Reference Publications:

1. W. A. Little, "Exciton Mechanism of Superconductivity", Low Dimensional Co-operative Phenomena. Ed H. J. Keller, p. 35 Plenum Press, New York (1975).

2. R. L. Greene, G. B. Street and L. J. Suter, "Superconductivity in Polysulfur Nitride $(SN)_x$", Physics Rev. Letters, Vol. 34 577 (1975).

3. M. N. Kronick and W. A. Little, "A New Immunoassay Based on Fluorescence Excitation by Internal Reflection Spectroscopy", Journal of Immunological Methods, to be published (1975).

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6. D. Whitmore, "One Dimensional Band Calculation of a Linear, Square Planar Platinum Complex", Physics Letters, 50A, 55 (1974).

37. EXPERIMENTAL AND THEORETICAL STUDIES ON ROCK-FORMING SYSTEMS AT HIGH TEMPERATURES AND PRESSURES

W.C. Luth, Associate Professor, Geology

Professional Associate

P. M. Fenn, Research Associate, Geology

Graduate Students

M. Naney

J. O'Brient

Agency Support

NSF GA 41731 (With W.A. Tiller and G.E. Brown)

Technical Objective

Experimental simulation, and analysis, of rock-forming processes taking place in the Earth's crust (outer 35 km) and upper mantle which involve interaction with, and crystallization from, silicate liquids in the presence, or absence, of an aqueous fluid phase.

Approach

Determination of phase stability in multi-phase, multi-component silicate-volatile systems at pressures to 10 kbar and temperatures to 1300°C. Characterization of materials by means of X-ray powder diffraction, optical, and electron microprobe techniques.

Research Report

(1) The system $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$.

P. M. Fenn

The feldspars, composed principally of the components listed above, are the most abundant minerals of the earth's crust. These minerals, plagioclase (Ca,Na) and alkali feldspar (Na,K) are capable of extensive crystalline solution, though limited by a miscibility gap or solvus. Most granitic rocks contain both plagioclase and alkali feldspar . Experimental studies are in process which are designed to provide direct data on the pressure, temperature, and bulk composition dependence of the compositions of the coexisting felspars.

(2) Phase Equilibria in Silicate-H_2O Systems; Volume Relations.

Analysis of available experimental P-V-T-Composition data on the system $NaAlSi_3O_8$ clearly demonstrates the necessity for explicit consideration of volume as a process variable in treating crystallization and melting relationships in natural systems. Most applications of experimental data to geologic systems involve an implicit assumption that the volume of the system is determined by the pressure (depth), temperature, and composition variables. If the volume of the system is constrained by the environment of crystallization (or melting) then estimates of the depth at which these processes occur in the natural environment, based on a variety of mineral equilibria, may be in error by 1-15 km.

(3) Crystallization of Ferro-Magnesian Phases from Granitic Liquids.

M. Naney

Biotite and hornblende are the common ferromagnesian phases found in the granitic rocks. Experimental studies on phase equilibria and kinetics of these phases from granitic liquids containing dissolved H_2O are continuing. These phases crystallize from liquids which are either saturated with, or undersaturated with, an aqueous fluid phase over a wide range of pressure and temperature. Consequently the presence of these hydrous, ferro-magnesian, phases in granitic rocks does not imply the necessary existence of an aqueous fluid phase at the time of crystallization.

Reference Publications

Steiner, J.C., R.H. Jahns, and W.C. Luth, "Crystallization of alkali feldspar and quartz in the haplogranite system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O at 4 kb" Bull. Geol. Soc. Amer., 86, 83-98, 1975.

Luth, W. C., "Theoretical Petrology". *In* Quadrennial report of the Volcanology, Geochemistry, and Petrology Section of the AGU to the IUGG, Transactions of the American Geophysical Union, 1975, in press

38. REACTIVITY OF SOLIDS

R. J. Madix, Associate Professor, Chemical Engineering

Graduate Students:

N.M. Abbas	I.E. Wachs
S.W. Johnson	D. Ying
D.Y. Ngan	

Agency Support:

NSF through CMR
ACS Petroleum Research Foundation
Research Development Fund
NSF Materials Division
NSF Chemical Processes Division

Technical Objective:

To elucidate the kinematics and chemical kinetics of reactive gas-solid collisions and the influence of surface structure and composition thereon.

Research Report:

(1) High Temperature Reactions of Solids

Graduate Student: D. Ngan

Molecular beam, low energy electron diffraction and electron microscopic techniques are being utilized to elucidate the kinetics and reactive collision processes occuring in high temperature gas-solid reactions. In particular, reactions are being studied in which the reaction products vaporize. These products can be detected mass spectrometrically. If the reactant gas is directed at the surface under study in the form of a modulated molecular beam, the products and the scattered reactant beam can be phase detected. The product phase lag is directly related to the kinetic rate constant. Thus, the reaction sequence occurring on the surface can be elucidated. Further information concerning the dynamics of the surface collision can be inferred from the spatial distribution of the unreacted portion of the scattered beam.

The oxidation of molybdenum with chlorine and oxygen-chlorine mixtures was studied extensively. Both lock-in phase and amplitude measurements and waveform analysis methods on the desorbing products were employed to understand the reaction process. The reaction sequence is complex, perhaps involving simultaneous solution of chlorine in the molybdenum and surface diffusion of oxygen. Further work is being done to define the physical processes operative in the reaction.

(2) The Effect of Surface Composition and Structure on the Formic Acid Decomposition of Ni(110)

Research Associate: Dr. T. Dickinson

Graduate Students: S. Johnson
N. Abbas
D. Ying

The primary objective of our research is to understand the role of surface compounds and structures on product selectivity, surface decomposition kinetics, sticking probabilities and inhibition by product species. Our approach is to use ultra-high vacuum methods for characterizing the above features of the surface reactivity; namely, we are employing Auger-Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), work function measurements, and flash desorption methods. We also wish to extend our studies to include ultraviolet photoemission spectroscopy. It is only fair to say that the connection between this type of work and "practical" catalysis is now unclear, but our work is conducted with this connection in mind. Our results to date indicate that these methods have great potential for studying fundamental problems in the catalytic conversion of coal gas to methane and methanol.

The decomposition of acetic acid on Ni(110) was studied in order to assess the generality of the behavior observed in the formic acid decomposition and to measure the systematic trends in the fundamental rate constants. As was the case with formic acid, acetic acid formed islands of adsorbate and decomposed autocatalytically. In addition adsorption of CH_3COOH at room temperature led to the formation of an acetic anhydride intermediate, further supporting the suggestion that formic anhydride forms on the surface in the decomposition of formic acid.

In addition the formic acid decomposition was studied on Ni(110)(2x1)O and an Ni/Cu(110) alloy surface (surface composition: 35% Ni, 65% Cu). In the latter study the results qualitatively resemble the decomposition on Ni(110)(4x5)C, suggesting chemical similarities between the catalytic properties of transition metal surface alloys with IIB metals and metal surface carbides. As these effects are due solely to surface compositional changes, they highlight the fact that the catalytic process is only secondarily sensitive to the electronic nature of the bulk of the solid.

(3) Molecular Beam Relaxation Spectrometry

Graduate Student: I. Wachs

The time response function observed for product molecules emitted from a solid surface from a square wave of reactant incident on the surface carries information about the surface reaction mechanism (reaction transform function). We were able to obtain waveforms for several reactions including

$$HCOOH \rightarrow CO_2 + H_2$$
$$H_2 + D_2 \rightarrow 2HD$$
$$CO_{ads} \rightarrow CO_{(g)}$$

as well as phase and amplitude information necessary to allow kinetic analysis. The exciting feature of this work is that it allows visual display of the surface transform function as the experiment is in progress, thus allowing the experimenter to find interesting regions of temperature and pressure for further quantitative study quite easily. It also opens up the possibility of waveform analysis for studying the kinetics and mechanism of reactions on well-defined surfaces.

The conventional approach to analyzing modulated molecular beam data has been by phase-sensitive lock-in detection, but we are finding that relaxation curves enhance our understanding of the surface processes. It has been stated many times in the chemical literature that the relaxation curves contain all of the kinetic information. To better understand these curves we have simulated many molecular beam experiments (simple adsorption desorption process, branched process, series process, and second order process) on the computer. The differences and similarities between the relaxation curves for these processes have been thoroughly investigated, and some of these results have already been applied to the decomposition of formic acid on Ni(110). Our studies of the formic acid decomposition on these surfaces indicate that the rate-limiting step changes from the decomposition on the surface (rupture of chemical bonds) to surface migration as the surface temperature is raised.

Reference Publications:

1. (with Falconer, J. and McCarty, J.) "The Explosive Decomposition of Formic Acid on Clean Ni(110)." Jap. J. Appl. Phys., Suppl. 2, Pt. 2, 525 (1974).
2. (with Ullman, A.Z.) "MBRS Studies of the High Temperature Oxidation of Polycrystalline Molybdenum: Surface Diffusion of Reaction Intermediates." High Temp. Sci. 6, 342 (1974).
3. (with Schwarz, J.) "Modulated Beam Relaxation Spectrometry: Its Application to the Study of Heterogeneous Kinetics." Surface Sci. 46, 317 (1974).
4. "Surface Microcatalysis by MBRS: Molecular Beam Waveforms." Surface Sci. 45, 696 (1974).
5. (with Falconer, J.) "Flash Desorption Activation Energies: DCOOH Decomposition and CO Desorption from Ni(110)." Surface Sci. 48, 393 (1975).
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39. ELECTROLYTIC DISSOCIATION OF NO_x EMPLOYING ZIRCONIA AND PROPERTIES OF THE NO_x-Pt-O SYSTEM

David M. Mason, Professor, Chemical Engineering and Chemistry

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*Received PhD during report period

Agency Support:

Department of Chemical Engineering Gift Funds

Research Report:

Zirconia stabilized with oxides of a cation of different valence from zirconia (e.g., CaO, Sc_2O_3, etc.) can have a very high oxygen ion conductivity allowing oxygen to be pumped from oxygen-bearing gases such as NO_x thus decomposing them. The rate of decomposition of the air-pollutant species, nitric oxide, to harmless species (via the reaction: $2NO \rightarrow N_2 + O_2$) was found to be markedly catalyzed on zirconia in the presence of an electrical potential. It is well known from this (Reference 4) and many other studies that bright platinum catalyzes NO decomposition. The catalytic decomposition of NO on Pt metal is inhibited by O_2, such behavior being attributed to preferential chemisorption of O_2 over NO as well as the possible formation of an inhibiting platinum oxide surface. The initial rationale for this investigation was the possibility that the decomposition of NO might be enhanced if O_2 were electrolytically "pumped" away from a Pt electrode deposited on zirconia, keeping the Pt oxygen-free. However, it was not anticipated that at high potentials dissociation rates 1000-fold that on non-porous Pt electrodes occur in the presence of either platinum or gold porous electrodes. Since gold is known not to catalyze NO decomposition, these results suggest that the catalysis is occurring mainly on a surface other than the platinum or gold, namely, on the zirconia surface itself. It is proposed that F-centers (or free electron sites) on the zirconia surface formed by the applied potential are primarily responsible for the observed catalysis.

The tremendous enhancement of the rate of NO decomposition in the case of porous platinum and gold has shown a convenient and powerful technique of reducing oxygen bearing species, viz., the injection of F-centers on the surface of the electrolyte at sufficiently high overpotentials. The dynamics of the system is being further studied with careful control of the electrode morphology by employing metal mesh. Also, the study is being extended to include other reactant gases such as CO of interest in fuel cells employing coal gases.

From a study of natural convection heat transfer in a chemically reacting system using a heated horizontal platinum wire in the ($2NO_2 \rightleftarrows 2NO + O_2$) system, the heat transfer rate has been found to increase rapidly when wire temperatures 750-850°C are reached. In an identical system except employing gold wires, no sudden increase in heat flux is observed. Since the decomposition of NO_2 is endothermic, it has been suggested that the increase in heat transfer rate might be due to the onset of a markedly catalyzed decomposition of NO_2. In keeping with this model, platinum in an environment of NO_2-NO-O_2 is covered by a protective, inhibiting coating of platinum oxide. At around 750-850°C, the oxide dissociates, thus exposing the clean catalytic platinum surface to the reactant NO_2.

If this model is correct, however, platinum dioxide would have to be stable at much higher temperatures than indicated by sparse information in the literature. One part of the investigation, then, dealt with the stability of the solid oxide(s) of platinum. Using a galvanic cell containing the solid electrolyte zirconia as an oxygen gauge, the equilibrium partial pressure of oxygen over platinum dioxide was measured in the temperature range 535 to

588°C. Using the same procedure, it was also determined that there is no stable bulk oxide of platinum between 650-800°C below 1 atm oxygen. It was shown that platinum dioxide, which is the most stable oxide, is stable only up to 583°C at 1 atm oxygen.

It was clear from these results that the bulk oxides of platinum cannot be responsible for inhibiting the decomposition of nitrogen dioxide on platinum. Published data on the decomposition of N_2O, and more recently of NO and formic acid on platinum also show that exposure to high oxygen pressure severely reduces the catalyticity of platinum. It is thus of interest to study the kinetics of the decomposition of NO_2 and to consider the effect of chemisorbed oxygen at high temperatures and high surface coverages.

In a second part of this investigation, the kinetics of the decomposition of NO_2 was measured using a thermal conductivity cell technique. Heat transfer in the conduction regime, as opposed to previous work using natural convection or forced convection (Reference 3), leads to a system of equations that can be solved numerically with sufficient accuracy for rate data to be extracted. Based on experimental conductivity data obtained with gold and platinum wires (together with numerical analysis, it is concluded that NO_2 decomposes at an appreciable rate on platinum heated above 750-850°C, the temperature at which the heat transfer rate rises sharply. Further evidence in support of this conclusion is provided by scanning electron microscopy which shows extensive etching of the platinum surface due to the rapid surface decomposition of NO_2. The decomposition rate was found to be proportional to NO_2 concentration, and inversely proportional to the square root of oxygen concentration.

In addition it was found from chemisorption measurements on Pt/SiO_2 that the platinum surface can be reconstructed when exposed to oxygen at high pressures and elevated temperatures. It is believed that the severe inhibition of the surface reaction at temperatures below 750-850°C is due to the presence of a reconstructed layer on the platinum surface. Heating above this temperature restores the standard platinum surface, which is much more active than the reconstructed surface in catalyzing the decomposition of NO_2.

Reference Publications:

1. S. Pancharatnam, R. A. Huggins and D. M. Mason, "Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen," Presented at the 145th Meeting of the Electrochemical Society, San Francisco, California, May 12-17 (1974); Accepted for publication in the Journal of Applied Electrochemistry, July 1975.

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3. B. G. Ong and D. M. Mason, "Catalytic Decomposition of Nitrogen Dioxide on a Heated Platinum Wire," Ind. Eng. Chem. Fundam. 11, 169 (1972).

4. S. Pancharatnam, K. Lim and D. M. Mason, "Catalytic Decomposition of NO on a Heated Platinum Wire," Accepted for publication in Chem. Eng. Sci., August, 1975.

5. Ngo, Tiong Gac, "Effect of Platinum-Oxygen Interaction on the Catalyticity of Platinum for the Decomposition of NO_2," Ph. D. Dissertation, Department of Chemical Engineering, Stanford University, Stanford, CA., December 1974.

40. PHYSICAL CHEMISTRY OF LIPID (OR LIPID/PROTEIN) BILAYER MEMBRANES AND OTHER SUPRAMOLECULAR COMPLEXES

H.M. McConnell, Professor, Chemistry

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Agency Support:

NSF BMS 75-02381
ONR N00014-75-C-0869

Technical Objectives:

To obtain a better understanding of the structure and function of biological membranes and other supramolecular complexes of biological origin.

Approach:

Protein complexes or model systems consisting of lipid (or lipid/protein) bilayers of well-defined composition, amenable to study by such physical techniques as electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR) and freeze-fracture electron microscopy, have been used (a) to develop technical methods suitable for such study and to investigate the fundamental physical chemical properties of membranes and other molecular complexes, (b) to attempt, and in some cases to demonstrate, correlation of biological functions such as ion transport, membrane fusion, complement fixation and receptor activity, with the physical state of the appropriate membrane constituents.

In addition, certain studies have involved the use of intact biological membranes, (i.e., erythrocyte).

Research Report:

(A) Development of EPR and NMR techniques and their use to investigate fundamental physical chemical properties of model membranes and other supramolecular complexes

(1) Saturation transfer EPR: slow rotational motion in biomacromolecular complexes.

Graduate Student: D.D. Thomas

Saturation transfer EPR of spin labels has been developed, theoretically and practically, as a unique method for measuring rotational motion in biomacromolecular assemblies for the time range $10^{-7} < \tau_2 < 10^{-3}$ sec, where τ_2 is the rotational correlation time. The motion of the S-1 region in myosin, and its supramolecular complexes, has been studied and quantitatively measured; the significance of this work is in regard to the molecular dynamics of muscle contraction. In addition, a study of the slow rotational motion of membrane components, specifically phospholipids and cholesterol (collective motion) and rhodopsin (the visual photoreceptor protein) has been commenced.

(2) Kinetics of phase equilibrium in a binary mixture of phospholipids by use of NMR spectroscopy.

Graduate Student: P. Brûlet

A 50:50 mole percent binary mixture of dipalmitoylphosphatidylcholine (DPPC) and dielaidoylphosphatidylcholine (DEPC) has been studied using ^{13}C nuclear magnetic resonance (25.2 MHz and 90.8 MHz). Each phospholipid was enriched in the choline methyl groups with ^{13}C. The line width of the ^{13}C resonance of the higher melting lipid (DPPC) in this binary mixture increases rapidly at temperatures below ~32 °C, the same temperature as determined earlier by spin label paramagnetic resonance and by freeze-fracture electron microsocpy to mark the onset of a lateral phase separation in the plane of the membrane. The temperature dependence of the observed ^{13}C line widths differs quantitatively but not qualitatively from theoretically calculated line widths based on the previously reported phase diagram for this mixture of lipids. The discrepancy may be due to density and composition fluctuations (nucleation) in the fluid phase of the lipids. Such fluctuations are suspected to be of importance for the transport of certain molecules through cell membranes.

(3) The use of freezing point depression, as monitored by EPR, to detect specific associations between membrane components.

Graduate Student: T. Lewis

If two molecular species, which independently depress the melting point of a solvent in an ideal manner, depart from this ideality when combined (by imparting a smaller depression than that which is calculated by simple summation), a specific molecular association is implied.

The chain melting temperature of phospholipids dispersed as bilayers in aqueous suspension have been measured by changes in solubility of the spin label, TEMPO, in the hydrophobic (lipid) environment, which are detected by EPR spectroscopy. Depressions caused by low concentrations of single species of impurities in phospholipid membranes, indicate ideal behavior. Work has commenced which aims at detecting specific associations between membrane components by the departure from ideality observed when low concentrations of two or more "impurities" are included.

(4) Fusion of phospholipid membranes.

Professional Associate: J. van der Bosch

In search for a suitable model system for biological membrane fusion, it was found that concanavalin A (a plant lectin, up to now thought to interact specifically only with certain sugar-containing receptors) interacts with pure dipalmitoylphosphatidylcholine (DPPC) vesicles. The interaction was investigated by means of EPR-spectroscopy, freeze etching and electron microscopy, as well as in collaboration with S. Aragon (Professor Pecora's lab.), by means of laser light scattering and analysis of the autocorrelation functions resulting from these experiments. It turned out that Con A binds to the vesicle surface, exerts in immobilizing effect on the membrane components and induces fusion of the vesicles resulting in extended membrane structures. The temperature dependence of the rate of the overall reaction, as measured ESR spectrocopically by application of a rapid mixing device, coupled to the capillary tube in the EPR-cavity, exhibits a pronounced maximum in the range of the phase transition of the DPPC-vesicles. This fact is interpreted in terms of density and structural fluctuations, which are maximum in the phase transition range. Regarding the structural possibilities of the DPPC molecule this interpretation offers a proposal concerning the basic molecular features of a general mechanism of lipid-membrane fusion.

(B) Isolation of membrane-bound proteins and their functional reconstitution

(5) Anion channel - protein III.

Graduate Student: A. Ross

Recently, we completed kinetic studies on the transport of an anionic spin label through the erythrocyte anion channel. We found that the rate of transport is strongly dependent on the transmembrane potential. We have isolated the anion channel and have preliminary results on its reconstitution. We hope to see the EPR signal of the spin label actually inside the anion channel. This would be an exciting discovery since there is no information on the physical state of any molecule during translocation.

(6) Microfilament protein - spectrin.

Graduate Student: E.J. Luna

The human red blood cell contains several structural proteins in approximately equimolar amounts. One of these, spectrin is a large filamentous protein which underlies the entire erythrocyte membrane and is believed to form part of a contractile system reminiscent of smooth muscle. In this laboratory, spectrin has been purified by previously described techniques and spin labeled. Its physical properties (alone in solution) and the interrelationships between spectrin, phospholipids and other erythrocyte membrane components are being studied by EPR and freeze-fracture electron microscopy.

(7) Human erythrocyte glycoprotein-glycophorin.

Professional Associate: C.W.M. Grant

Glycophorin, the major glycoprotein of human erythrocytes, has been isolated and reincorporated into lipid vesicles. Freeze-fracture electron microscopy shows the reincorporated glycophorin to occur as small particles in vesicle fracture faces while the etch faces are smooth.

The glycoprotein has a tendency to cluster into groups of several particles. Evidence is presented that, although lipids in immediate contact with glycophorin are likely somewhat immobilized, the entire lipid-protein complex has a tendency to occupy fluid regions of the bilayer. Reincorporated glycophorin assumes its proposed conformation in the intact erythrocyte in so far as it penetrates the hydrophobic membrane interior while its N-terminal end with attached carbohydrate residues is exposed to the aqueous compartment and is available as a specific recognition site.

(8) ATP'ase from rabbit sarcoplasmic reticulum.

Graduate Student: W. Kleemann

Mixtures of lipids and protein, the ATPase isolated from rabbit sarcoplasmic reticulum, were studied by freeze-fracture electron microscopy and by measurement of the amount of fluid lipid with the spin label TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl). In dimyristoyl phosphatidylcholine vesicles the protein molecules were randomly distributed above the transition temperature, T_t, of the lipid and aggregated below T_t. For mixtures of dimyristoyl- and dipalmitoylphosphatidylcholine the existence of fluid and solid domains was shown in the temperature interval predicted from earlier TEMPO measurements. When protein was incorporated into this lipid mixture, freeze-fracture particles were randomly distributed in fluid lipids, or aggregated when only solid lipids were present.

In mixtures of dimyristoylphosphatidylcholine with cholesterol the protein was distributed randomly above the transition temperature of the phosphatidylcholine. Below that transition temperature the protein was excluded from a banded phase of solid lipid in the case of 10 mol% cholesterol. In mixtures containing 20 mol% cholesterol protein molecules formed linear arrays, 50 to 200 nm in length, around smooth patches of lipid.

Phase diagrams, applicable to the bilayer, were used to interpret the observations. They are essentially of the eutectic type, the protein molecules being excluded from solid lipids and being incorporated into the eutectic. Increasing solidification around protein molecules without formation of a separate phase above the transition temperature of the lipid must be invoked to explain decreases in TEMPO solubility. Cholesterol shows a behavior analogous to protein.

(D) The use of EPR spectroscopy to monitor physical changes occurring in the membranes of biological cells.

(9) Hormones and cyclic nucleosides: effects on erythrocyte membranes.

Professional Associate: P.G. Kury

We have used spin labels to detect prostaglandin E induced changes in erythrocyte membranes. The observed changes in spin label resonance spectra can be mimicked in erythrocyte ghosts by loading them with cyclic adenosine monophosphate or cyclic guanosine monophosphate. These changes can also be observed by adding either of these cyclic nucleotides to intact cells. This entry of cyclic nucleotides into intact cells is blocked by an inhibitor of the anion channel. We suggest that the observed changes in paramagnetic resonance spectra are due to changes in lipid "fluidity" that are brought about by changes in the biochemical state of membrane-associated proteins (such as spectrin) and in the direct or indirect biophysical interaction of these proteins with membrane lipids.

(E) Immunochemistry of membranes

(10) Complement fixation and immune lysis as a function of the physical state of membrane antigens.

Professional Associates: G.M.K. Humphries
J. Murdoch

The complement fixing activity of liposomes containing cholesterol, dimyristoylphosphatidylcholine (or dipalmitoylphosphatidylcholine), and 3 mol% of cardiolipin has been studied as a function of cholesterol concentration by use of human syphilitic serum containing cardiolipin-specific (Wasserman) antibodies. It is found that complement fixation increases rapidly for cholesterol concentrations above 35 mol%.

Spin label studies have been used to study the incorporation of cardiolipin in the relatively rigid phase of binary mixtures of cholesterol and dimyristoylphosphatidylcholine (or dipalmitoylphosphatidylcholine). It is concluded that cardiolipin is included in such a phase of these lipids for cholesterol concentrations above 35 mol%.

These results indicate that a relatively rigid lateral distribution of this monovalent antigen in the plane of the membrane facilitates complement fixation and concomitant complement-mediated membrane damage.

Work is in progress concerning the complement fixing activity of glycophorin reconstituted in lipid bilayers, together with anti-glycophorin (IgG fraction).

Work is also in progress concerning the effect of cytochalasin B on the immune lysis of sheep red blood cells.

PUBLICATIONS

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P.G. Kury and H.M. McConnell, "Regulation of Membrane Flexibility in Human Erythrocytes", Biochemistry, in press.

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41. INTEGRATED ELECTRONICS

J.D. Meindl, Professor, Electrical Engineering

Professional Associate

J.D. Plummer

Graduate Student

M.D. Pocha

Agency Support

NIH 1 P01 GM17940-05 GMP
NSF ENG74-18419

Technical Objective:

To investigate new materials, structures and processing techniques for improving the performance of monolithic integrated circuits, novel biomedical applications of these devices are of particular interest. Many of these biomedical systems employ transducers (piezoelectrics are one example) which require high voltage integrated circuits to drive them. Integrated circuits of this type are not available from commercial manufacturers and hence custom integrated circuits with unusual properties are required.

Approach:

The high voltage integrated circuits required in many biomedical systems employing transducers of a piezoelectric or other nature, are not available commercially primarily for two reasons. First, a good high voltage MOS transistor has not been readily available. Second, unwanted parasitic interactions between devices at high voltage levels have hampered the integration of many devices in a monolithic substrate. Solutions to both these problems have been found and a new high voltage integrated circuit technology has been developed.

Research Report:

Progress in the design, fabrication and performance of integrated circuits and integrated circuit devices in the past several years has occurred along a broad front. Digital circuit switching speed, power consumption and power-speed product have all seen dramatic improvement. Linear circuit frequency response and power consumption have similarly been greatly improved.

Similar progress has not occurred in high voltage integrated circuits. This is not so much because of lack of applications for such circuits, but primarily because of device limitations and because of interaction problems which arise when many high voltage devices are placed together in a monolithic substrate.

Conventional MOS transistors have voltage limitations which are inherent to the device structure. Essentially all commercially available MOS integrated circuits are specified with maximum sustaining voltages of 30 volts or less. The principal reason for this is that in a conventional MOS transistor very high electric fields exist, even at moderate voltages, in the region where the drain junction underlies the thin gate oxide. Surface breakdown of the drain junction results at relatively low voltages and is virtually unavoidable in standard MOS structures [1].

A number of attempts have been made to modify the standard MOS structure to improve the device's surface field limited breakdown. None have found wide industrial acceptance.

The double-diffused (DMOS) transistor [2] represents a new solution to this problem. The device is fabricated very much like a bipolar NPN transistor. Two sequential diffusions, first P type and then N type are done through the same oxide window. The difference in lateral spread of the two diffusions forms the channel region of the device. Channel lengths of 1μ to 3μ are easily possible with this structure, resulting in a transistor that is a very fast switch (sub-nanosecond switching speeds), has low ON resistance (as low as a few ohms), and can carry large currents (several amperes). Because the channel lengths are so short in these devices, the carriers in the channel can travel at the scattering velocity limit of ≈ 10^7 cm/sec in silicon. This results in the transconductance of the device being independent of current under appropriate gate and drain voltage conditions. DMOS transistor breakdown voltage can also be very high (> 300 volts), principally because the drain depletion region spreads into the lightly doped N^- substrate and not into the more heavily doped P channel region. Regions of high electric field are therefore kept away from the thin oxide channel portion of the device.

DMOS devices and technology have been developed in the Integrated Circuits Laboratory and have been used as the basis for a new high voltage integrated circuit technology. This new technology has greater flexibility and higher performance than any other reported high voltage technology. Its principal features are as follows:

1. A wide variety of components including N channel MOS (DMOS), P channel MOS (both thin and thick oxide), vertical NPN and lateral PNP bipolar transistors, JFETs and a variety of resistors are all compatible with the new technology. A number of integrated circuits have been built using these components. The new high voltage technology requires only 7 masking steps and no critical or difficult steps.

2. Integrated circuits fabricated with this new technology have been operated at voltages in excess of 250 volts. This represents almost an order of magnitude improvement over similar function commercially available parts.

3. High switching performance has not been sacrificed to achieve the high voltage operation. For example, one circuit built with this technology utilizes N channel DMOS and P channel MOS devices in a complementary MOS configuration. This particular circuit functions as a level translator and can switch states between + 75 and - 75 in approximately 100 nsec.

4. High current capability in the DMOS devices has also been achieved. Devices approximately 1/2 mm square have been fabricated which can carry peak currents of roughly 0.5 amperes. These devices at the

same time exhibit breakdown voltages greater than 250 volts and have been used in a number of our biomedical systems for transducer driving.

Further details and figures relating to this development are contained in references 3 and 4.

In summary, the new and significant results reported are:

1. A reproducible technology has been developed for fabricating high voltage, high performance DMOS transistors.
2. This technology has been generalized to make it into a general purpose high voltage technology with a wide variety of MOS and bipolar devices capable of being integrated on the same silicon chip. This new technology has been used to fabricate a number of high voltage ICs and has greater flexibility and higher performance than any other reported high voltage technology.

Reference Publications:

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3. J.D. Plummer, J.D. Meindl and M.G. Maginness, "A New Ultrasonic Imaging System for Real Time Cardiac Imaging," ISSCC Conference Digest, Feb. 1974.

4. M.D. Pocha, A.G. Gonzalez and R.W. Dutton, "Threshold Voltage Controllability in Double-Diffused MOS Transistors," IEEE Trans. Electron Devices, ED-21, Dec. 1974, pp. 778-785.

42. RELATIONS BETWEEN CRYSTALLINE IMPERFECTIONS AND THE PHYSICAL PROPERTIES OF CRYSTALS

William D. Nix, Professor, Materials Science and Engineering

Graduate Students:

M. A. Burke
R. J. DiMelfi*
J. C. Gibeling
P. S. Gilman
S. H. Goods
J. H. Holbrook
R. W. Lund
T. C. Reiley*
J. R. Spingarn

* Received Ph.D. during report period

Agency Support:

ERDA E(04-3) 326 PA-17
NSF GH-34358
AFOSR-73-2434
NSF through CMR

Technical Objective:

To understand and exploit the relation between imperfections and the physical properties of crystalline solids. To develop techniques for predicting and controlling the mechanical and electronic behavior of crystalline materials in order to establish guidelines for making both structural and electronic materials.

Approach:

To carry out both theoretical and experimental investigations of crystalline solids with known concentrations of various types of defects.

Research Report:

(1) Application of Finite Element Techniques to Problems Involving Creep, Plastic Instability and Fracture of Metals

Graduate Student: M. A. Burke

Research efforts have been concentrated on developing techniques to analyze the macroscopic and microscopic aspects of plastic instability during high temperature deformation. Computer based simulations have been devised for this purpose using finite element analysis techniques. Two algorithms have been developed to model elastic-plastic deformation. One program simulates the time independent plastic deformation of an isotropically strain hardening material as well as the time dependent plastic deformation of solids that are elastically constrained. The program is capable of analyzing orthotropic and composite materials with time and temperature dependent properties and simulating both monotonic and cyclic loading. A second finite element program was developed to analyze inhomogeneous and finite viscoplastic deformation associated with instability during tension creep. Studies are currently being made to simulate the macroscopic instability that occurs in tensile creep test specimens and the microstructural instability that arises when grain boundary triple point cracks develop and grow by the coalescence of microvoids. This program when fully developed will also be able to analyze some aspects of high temperature/high strain rate deformation associated with metal working.

(2) A Theoretical Study of High Temperature Failure Mechanisms

Graduate Student: R. J. DiMelfi

It has often been observed in practice that materials fail at high temperatures by the growth and coalescence of internal voids. It has also been noted experimentally that the rupture and deformation processes are related. We have been engaged in a theoretical study of this problem.

The basic approach has been to determine the growth behavior of holes in viscous media under uniaxial tension. The choice of a linearly viscous continuum allows us to solve certain of these problems analytically by applying a special simple case of the elastic-visco-elastic analogy to the elasticity solutions. Using this technique for single hole geometries has convinced us that a realistic model of ductile rupture must include the consideration of the interaction between holes.

In order to consider the effects of void interaction we have generated the solution for two circular holes in a plane viscous medium under axial tension applied normal to their common axis. This solution gives us information about the initial growth behavior of the holes as a function of applied stress and hole spacing. In addition, the complex variable technique employed allows us to follow the hole growth during shape changes analytically. It is expected that the model developed in this way will aid in understanding some of the problems related to high temperature creep failure.

(3) The Unloading Technique for Measuring Internal Back Stresses

Graduate Student: J. C. Gibeling

The measurements of internal back stresses which develop during high temperature deformation was first performed at Stanford several years ago. Since that time, this concept has gained fairly widespread acceptance and has even found some application in design considerations. During recent years, however, significant criticism and doubt has arisen regarding the validity of these measurements.

The most popular technique for measuring the back stresses which act on dislocations in a deforming sample is the strain transient dip test. Here, a specimen undergoes creep until a steady-state rate is reached. At this point a portion of the load is removed, and the strain transient is observed. From the observed behavior, one can distinguish between two basic models of the dynamics of dislocation motion.

Our present work is aimed at maximizing the accuracy and sensitivity of this test in order to remove ambiguities which have previously existed in these observations. The three conditions which must be met are high strain resolution (1 microstrain), high time resolution (less than 0.1 seconds) and high unloading rates. To meet these requirements, our approach is to use resistance strain gages applied directly to the deforming sample, an oscillograph to record the output, and a nylon string which is burned to remove the load. Further, we are using lead specimens so that the deformation may conveniently be carried out at room temperature.

To date, this technique has been successfully applied to polycrystalline samples of lead. Analysis of the results indicates that they cannot be easily characterized in terms of a simple analytical model. Work is presently proceeding to apply the same technique to single lead crystals, so that the influence of grain boundaries can be eliminated.

(4) Investigation of the Processing Techniques of Dispersion Strengthened Metals

Graduate Student: P. S. Gilman

Detailed studies of the high temperature deformation of dispersion strengthened metals have been made. However, in regards to the processing of these metals, studies have only produced certain empirical facts and the current processing methods are still largely guided by intuition. This research is directed at gaining an understanding of the mechanisms associated with the processing of these metals with the hope that a fundamental study of the mechanisms of processing would help guide the manufacture and use of dispersion strengthened metals. Factors to be studied are grain boundary mobilities and crystallographic textures in these materials as well as the effects associated with the recrystallization of these materials.

The first and current stage of this investigation is a thorough search of published literature and industrial reports, augmented with direct industrial contact of the current state of knowledge concerning the processing of dispersion strengthened metals. With this knowledge we plan to simulate various processing techniques on model materials in order to investigate the various mechanisms of processing. One processing method to be explored is mechanical alloying which will utilize the Materials Science and Engineering Department's new attritor, high energy ball mill, to finely fragment the alloying elements used in the manufacture of dispersion strengthened metals.

Finally, the results of this research will give a much clearer picture of the important variables involved in the successful manufacture of dispersion strengthened metals.

(5) The Effects of Gas Bubbles and Voids on the Tension Creep Properties of Metals

Graduate Student: S. H. Goods

In an effort to further understand the structure dependence of high temperature deformation, we are examining the effects of inert gas bubbles and voids on the tension creep properties of silver. The embrittling mechanisms of a bubble or void microstructure are important as it is known that the mechanical properties of various fission reactor components degrade with time due to the formation of inert gas (He) bubbles.

Various procedures for introducing bubbles and voids have been investigated. The method chosen (because of its relative simplicity) involves the annealing of high purity silver in a variable oxygen atmosphere followed by a hydrogen anneal. In this way, water vapor bubbles, chemically inert with the silver, are produced. The water vapor is found to nucleate both heterogeneously and homogeneously in silver, as does helium in structural metals within nuclear reactors. The bubble size and distribution is controlled by varying the partial pressures of the annealing atmospheres and annealing times.

The mechanical testing program has been recently initiated and the main emphasis here is to collect data on the untreated silver although tension creep tests on silver containing bubbles will begin shortly. It is hoped that a complete study of the effects of these bubbles on silver can be extended to further develop a general model for grain boundary cracking and brittle failure in metals in the presence of these microstructural defects.

(6) A Study of Creep of Dispersion Strengthened Single Crystals

Graduate Student: J. H. Holbrook

Research efforts have consisted of two aspects of the study of dispersion strengthened metals. One aspect consisted of testing dispersion strengthened single crystals in constant stress creep tests. Single crystal specimens were used in order to differentiate between strain contributions from grain deformation and grain boundary sliding (gbs). These both occur in polycrystalline metals containing a dispersed, hard second phase. In some metal systems a large percentage of the creep strain comes from gbs, thus a stronger material could result by eliminating grain boundaries.

The metallic system selected for testing was a precipitation hardenable binary system of approximately one per cent silicon in aluminum. The precipitate is pure silicon, and because of its strength, stiffness, and incoherency it behaves much like a mechanical dispersoid. Creep tests of single crystals of aluminum with precipitates of silicon demonstrated strengths equivalent to those of polycrystalline Al-Si of equivalent volume fraction of silicon or better. Tests showed differences in creep stress dependence in high and low stress regimes. The transition stress is understood to be the Orowan bowing stress for the material.

The second aspect of this research has involved an analytical examination of dislocation-dispersoid interaction. Topics considered were: effect of elastic mismatch between matrix and particle on stress dependence of climb-controlled creep; enhanced climb of edge dislocations when bent into a screw configuration between particles; statistical effects of particle clustering upon dislocation glide; effects of stacking fault energy on mobile dislocation density; and creep contribution from diffusive movement of small dispersoids. These problems required extensive computer usage in simulating dislocation motion.

(7) High Temperature Creep of Ni-20Cr-2ThO$_2$ Single Crystals

Graduate Student: R. W. Lund

Single crystal tensile samples were cut from blocks of Ni-20Cr-2ThO$_2$ having large elongated grains. These samples were tested at varous temperatures from 650°C to 1300°C and various stresses from 9500 psi to 55000 psi under constant stress vacuum creep conditions. Results of these tests have been beneficial in providing supportive evidence for two hypotheses which explain (a)heretofore anomalously high creep activation energies reported by many previous investigators for dispersion strengthened metals and (b) heretofore unexplained high stress dependence of dispersion strengthened metals.

We believe that the high creep activation energies result from neglecting the temperature dependence of the elastic modulus of the material. This modulus correction to the apparent creep activation energy is particularly important for materials having a high stress dependence (large stress exponent). Our calculations indicate that these anomalously high activation energies can be corrected to activation energies equal to those for self diffusion, as is the case for pure metals and many alloys.

We have also found that the high stress dependence of this material can be understood in terms of an assymptotic approach of the flow stress for the Ni-20Cr-2ThO_2 to the Orowan bowing stress. That is, at a particular temperature and strain rate, the steady state flow stress in Ni-20Cr-2ThO_2 can be predicted by adding the steady state flow stress of Ni-20Cr to the calculated Orowan bowing stress of the Ni-20Cr-2ThO_2. The predicted strain rate is found to agree within an order of magnitude with the strain rate determined experimentally.

We have also found that the very high temperature creep strength of this material is limited by diffusive coarsening of the ThO_2 particles. This limit is governed by the relationship between the kinetics of particles coarsening and the average interparticle spacing (which defines the Orowan stress).

(8) Structure and Mechanical Properties of Physically Vapor Deposited Cr

Graduate Student: T. C. Reiley

The structural and mechanical characteristics of physically vapor deposited thick films (~1mm) have been studied. They are produced by electron beam evaporation of Cr ingots with subsequent condensation over a range of temperature (150°C - 1100°C), rate of deposition (1000 - 4000 Angstroms/sec), and pressure (10^{-5} - 10^{-7}torr).

The extremely high deposition rate allows the production of highly non-equilibrium structures. In the case of PVD Cr, material with a submicron grain size has been produced; this is two orders of magnitude finer grain size than that created by normal processing.

With a firm theoretical and experimental basis, it was expected that our production of fine grained chromium would lead to considerable reduction in the notoriously high ductile-brittle transition temperature

(DBTT) in the recrystallized condition. However, it appears from density and microstructural examination that under accessible evaporation conditions material is produced with a large number of grain boundary cracks and macroscopic defects, leading to poor mechanical properties.

(9) Creep of Fine Grained Materials

Graduate Student: J. R. Spingarn

We are studying the creep behavior of the fine grained materials at low stresses. Although the theoretical predictions of Nabarro and Coble are well known, direct experimental evidence is in short supply. We suspect that this regime may be crucial to understanding the role of grain boundary processes in sliding or superplastic materials. A second application we will explore is the effect of grain boundary density on mechanical properties when large defects such as radiation induced voids are introduced.

In order to obtain grain sizes in the range 1 - 10 μm we are using high rate physical vapor deposition on high purity Al, Cu, and Ni, as well as codeposits of these metals with Al_2O_3. To utilize the large body of accumulated data on elastic modulus and self diffusion, we are concentrating on predominantly single element systems. As part of this study we are investigating the effect of processing variables such as temperature, composition, substrate chemistry and deposition rate on the microstructure of the deposits.

Early results indicate that the creep strength of vapor deposited materials is higher than conventional materials, while the ductility depends sensitively on the microstructure.

Publications:

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2. R. A. Menezes and W. D. Nix, "High Temperature Dislocation Mobility in LiF; Part I Charged Dislocations in Ionic Crystals", Materials Science and Engineering, 16, 57 (1974).

3. R. A. Menezes and W. D. Nix, "High Temperature Dislocation Mobility in LiF; Part II Glide Mobility of Dislocations at High Temperatures", Materials Science and Engineering, 16, 67 (1974).

4. J. H. Holbrook and W. D. Nix, "Edge Dislocation Climb Over Non-Deformable Circular Inclusions", Met. Trans., 5, 1033 (1974).

43. SEISMIC VELOCITIES OF LOW-POROSITY ROCKS AT HIGH PRESSURES AND TEMPERATURES

A. M. Nur, Associate Professor, Geophysics
W. C. Luth, Associate Professor, Geology

Graduate Student:

J. W. Spencer (received PhD degree during report period)

Agency Support:

Chevron Oilfield Research Company

Technical Objective:

To study compressional and shear wave velocities in Westerly granite under conditions of high temperature to 500°C, high pressure to 5 kb, and independently controlled pore water pressure.

Approach:

Piezoelectric ultrasonic transducers are used to measure the travel times of waves passing through the jacketed rock samples, in an experiment which operates inside an internally-heated, argon-medium pressure vessel. We control independently pore fluid pressure inside the jacketed sample, temperature and confining pressure.

Research Report:

This is the final report on a completed project. Measurements in a dry sample show that at a given temperature, confining pressure has a larger accelerating effect on compressional waves, while, at a given confining pressure,temperature has a larger retarding effect on shear waves. The combined effects of temperature and pressure therefore act to increase Poisson's ratio with depth in a dry earth. Increasing the temperature of a low pressure pore fluid causes a continuous, marked decrease in k and Vp, while μ and V_s are affected only by the temperature of the crystalline matrix. The low V_p and nearly unchanged V_s cause a marked decrease in

Poisson's ratio. A high pressure pore fluid causes a marked decrease in μ and V_s, while V_p is less affected, and Poisson's ratio increases. Gassmann's theory, for the elasticity of saturated porous media, is found to closely predict saturated samples' compressional and shear velocities from the elasticity of their crystalline matrix and the known properties of water.

44. RECRYSTALLIZATION OF QUARTZ UNDER NON-HYDROSTATIC STRESS

A. M. Nur, Associate Professor, Geophysics

Graduate Student:

E. S. Sprunt

Agency Support:

Chevron Oilfield Research Company
NSF (Graduate Fellowship)

Technical Objectives:

To understand the process of pressure solution in porous rocks. The program consists of two main parts: (1) a study of solution and redeposition of silica in an aggregate material -- sandstone, as a function of pore pressure and confining pressure, and (2) a study of the effect of stress on a single cavity in a rock.

Approach:

A jacketed hollow cylinder of the quartz aggregate is subjected to various combinations of pore and confining pressure at 340°C for about 250 hours. The samples are then carefully examined using a luminoscope as well as standard petrographic techniques. The single pore is modeled by a circular hole drilled ultrasonically in a slab of novaculite-cryptocrystalline quartz. The slab is placed in a pressure vessel so that 150 bars of water pressure can be maintained at 260°C while the sample is subjected to a load perpendicular to the axis of the hole. The eccentricity of the hole is measured as a function of load and time.

Research Report:

A shaking-heating pressure vessel unit has been assembled for the hollow cylinder experiments. The system is operational, and experiments are currently in progress. An axial load vessel for the single cavity experiments has been designed and built. The problem of sealing around the piston at 260°C has been solved. Further modification of the apparatus may be necessary, but preliminary experiments indicate that measurable changes in the eccentricity of the hole can be obtained in times of less than 100 hours.

45. NONLINEAR OPTICAL EFFECTS

R. H. Pantell, Professor, Electrical Engineering

Professional Associates:

M. A. Piestrup
G. B. Rothbart*
R. Powell

*Received Ph.D. during report period

Graduate Students:

R. Baumgartner
Chi Keng Chen
J. Ramos-Salas
R. N. Fleming

Agency Support:

NSF-ENG-71-02378-A01
NASA NGS-7110
NSF-ENG-75-02403

Technical Objective:

1. To obtain sources of far infrared, vacuum ultraviolet, and soft x-ray emission for materials research.
2. Construct an optical klystron.

Approaches:

1. Develop a Cerenkov light source that provides a continuum of radiation from far infrared wavelengths to 600 Å and to use this emission for various spectroscopic studies.

2. Develop tunable, optical amplifiers, oscillators and harmonic generators based on the principle of the klystron that operates in the ultraviolet and soft x-ray regions of the spectrum.

3. Generate tunable far infrared radiation from the stimulated Raman effect using various crystals.

Research Report:

(1) Vacuum Ultraviolet Emission from Cerenkov Radiation

Graduate Students: Chi Keng Chen, D. Baumgartner

The spectral power density from Cerenkov radiation in the vacuum ultraviolet was measured using helium as a Cerenkov radiator. A bright tunable source of vacuum ultraviolet radiation from 2000 Å to 620 Å was observed with peak power on the order of a milliwatt. The experimental values match the predicted theoretical ones quite closely.

Few continuum sources of radiation exist in the vacuum ultraviolet portion of the spectrum, particularly for wavelengths shorter than 1000 Å. During the past decade synchrotron sources have been developed to encompass the range from infrared to hard x-rays. Cerenkov radiation is an alternative means for providing high intensity vacuum ultraviolet to 600 Å. A comparison between the spectral power density (measured in power per unit wavelength per electron) from Cerenkov and synchrotron radiation shows that the former is two to three orders of magnitude greater in the vacuum ultraviolet.

(2) Continuously Tunable Submillimeter Wave Source

Graduate Student: R. N. Fleming

A method for spanning the 100 to 1000 μ portion of the spectrum with continuous tunable coherent radiation has been developed. The approach is based upon laser light scattering from the long-wavelength side of the A_1-symmetry soft mode in $LiNbO_3$. In contrast with other techniques, this method uses a single fixed-frequency pump source, requires no magnetic field, provides continuous rather than discrete tuning, can cover most of the 100 to 1000 μ range, operates at room temperature, and is simple to tune. The experimental data show that tuning was obtained from approximately 150 to 700 μ.

Reference Publications:

M. A. Piestrup, R. N. Fleming and R. H. Pantell, "Continuously Tunable Submillimeter Wave Source," Appl. Phys. Lett. 26, 8 (1975)

(3) Nonlinear Interactions of Relativistic Electrons and Radiation in Matter.

Graduate Student: J. Ramos-Salas

In this work the possibility of using stimulated emission of two photons from a free electron beam is considered for obtaining laser action in a wide region of the spectrum from the far infrared up to x-rays. The rate equation for the process has been determined and the gain calculated for the process to occur. The gain is generally low in the visible and x-ray region of the spectrum. However, some gain may be possible especially in the microwave region if intense electron currents are used.

(4) An Optical Klystron

Graduate Students: D. Baumgartner, Chi Keng Chen

Coherent energy exchange between a laser and a relativistic electron beam may occur by having the interaction take place in a medium for which wavevector synchronism exists, i.e., the electron remains in a field of constant phase. We have measured approximately 40 KeV momentum modulation of a 100 MeV electron beam by a 1 MW Nd:YAG laser. Having demonstrated momentum modulation of an electron beam, the next step is to achieve optical bunching. A Monte Carlo computer simulation has been performed and is presently in operation to demonstrate the possibility of optical bunching. The preliminary results indicate that bunching is possible. Experimental verification is now planned in the near future.

Reference Publications:

M. A. Piestrup, G. B. Rothbart, R. N. Fleming, R. H. Pantell, "Momentum Modulation of a Free Electron Beam with a Laser," J. Appl. Phys. 46, 1, (1975).

46. PHYSICS AND CHEMISTRY OF OXIDES AND OXIDE SURFACES

G. A. Parks, Professor, Applied Earth Sciences

Graduate Students:

P. V. Avotins*
R. P. Ebro
R. M. Railey
L. J. McAllister
M. T. Utine*

* Received Ph.D. during report period

Agency Support:

NSF GI 40614 (RANN-trace contaminants, terminated 28 February 1975)
NSF through CMR

Specific Adsorption of Aqueous Solutes onto Solids

Recently developed, largely theoretical, adsorption isotherms account well for the pH dependence of the adsorption densities of several metal ions and their hydrolysis products onto simple oxides. They permit a considerable degree of prediction and are able to account for inorganic complexation of the adsorbate but do not account for variability of the solid phase.

Technical Objective:

(1) To extend existing isotherms to accomodate a variety of complexes of mercuric ion during adsportion onto Fe_2O_3 in H_2O.

(2) To determine, through a study of the adsorption of a single metal onto several solid substrates, whether variability can be attributed primarily to differences in specific surface area or, if not, what direction investigation of variability should take.

Approach:

(1) Mercury forms a well characterized set of hydroxo- and chloro-complexes. Knowledge of its adsorption behavior is needed in a study of its environmental chemistry and in pollution abatement technology development. Through experimental comparative study of the adsorption of mercury by freshly

precipitated hydrous Fe(III) oxides and their well crystallized, aged counterparts we hope to gain some insight into sources of variability and differences between co-precipitation and true adsorption.

(2) Modification of existing adsorption isotherms to accommodate more than one set of complexes and competitive adsorption among cations.

Research Report:

Experimental Adsorption Isotherms for Hg(II) on Selected Solids. Modelling. (All of this work has been done by P. V. Avotins in collaboration with E. Jenne of the U.S. Geological Survey, and J. O. Leckie of the Civil Engineering Department).

The adsorption of mercury on hydrous iron oxides is a small contribution to better understanding of the fate of mercury in the environment. The distribution of mercury in natural systems is affected by a tendency of mercury to adsorb from the aqueous phase onto solids. Since iron oxide is abundant in various lake and stream sediments, it is an appropriate substrate for the adsorption study.

A preliminary investigation was conducted to insure that mercury was not lost from aqueous solution by means other than sorption on the oxide. This work was extended to study the time stability of dissolved mercury in water samples. It is probable that many published values for mercury content in fresh waters err on the low side because of the rapid rate of loss which may take place after the waters are sampled. Various sample preservation techniques have been proposed but most are inadequate because biological effects have been overlooked. Data from our experiments indicate that the rate of mercury loss was higher from solutions containing bacterial activity than from sterile solutions. Only a fraction of the mercury loss was attributable to the amount adsorbed on the walls of the sample container. Additionally, in the samples with bacterial activity, the amount of mercury remaining in solution after a ten day storage time is a linear function of the concentration of mercury in the non-volatile form. As a result of unpredictable growth of bacterial populations, mercury may vaporize, bind to the walls of the vessel, or be stabilized in aqueous solution.

The kinetics of the mercury sorption reaction must be established to ascertain that equilibrium has been reached in the experiments, and to determine whether equilibrium is likely in natural systems. The experimental data indicate that sorption of mercury by hydrous iron oxide is a multi-step process. A fast step, during which about 70 percent of the mercury is adsorbed, is followed by continued mercury uptake, lasting for a duration of three months or longer. There are several lines of evidence that the second, slower step, is due to diffusion of mercury through the hydrous oxide. The diffusion coefficient of mercury in hydrous iron oxide was an order of magnitude higher in experiments conducted at pH 6.5 than those at pH 11. The reported difference in equilibrium adsorption densities at these pH values may be due to kinetic effects.

The pH dependence of the fraction of mercury adsorbed is similar to that observed for other multivalent cations. Little adsorption is observed at low pH. As pH is increased, a sharp increase in the fraction adsorbed occurs at a pH characteristic of the adsorbing ion. For mercury, in a system free of chloride or organic ligands, the sorption edge occurs at pH of about three. This is the pH at which mercuric hydroxide becomes the predominant mercury species. The effect of certain ligands, such as chloride, is to supress adsorption over a portion of the pH range. The location of the adsorption edge on the pH scale depends upon the chloride concentration. Experimental evidence showed that this location coincides with the apparent change in predominant mercury species from mercuric hydroxide, an adsorbing species, to mercuric chloride, a non-adsorbing species.

An exchange model was found to satisfactorily describe the dependence of the adsorption density on concentration of mercury in solution, pH, chloride, and ionic strength. The exchange constant for the overall adsorption reaction is 0.068. Utilizing this data together with mercury hydrolysis constants, the equilibrium constant for adsorption of mercury by hydrous iron oxide is 20,600. The free energy of adsorption for the process is -5.92 kcal per mole.

Competitive Adsorption Among Cations

The type of exchange adsorption isotherm used by Avotins are derived from reactions, such as;

$$M^{+2} + S'N \overset{K_1}{=} N^{+2} + S'M \qquad (1)$$

and

$$M^{+2} + 2(SH) \overset{K_2}{=} 2H^{+} + SM \qquad (2)$$

in which M^{+2} and N^{+2} are metal ions and S' and S are surface sites available for adsprption. In principle the equilibrium constants for these reactions are related, thus if

$$K_1 = K_M^N = \frac{\Gamma_M(M^{+2})}{\Gamma_N(N^{+2})} \qquad (3)$$

and

$$K_2 = K_M^H = \frac{\Gamma_M(H+)^2}{\Gamma_H{}^2(M^{+2})} \qquad (4)$$

K_1 should be

$$K_M^N = K_M^H/K_N^H \qquad (5)$$

We have just started a study of competitive ion exchange using Ca^{+2}, Cu^{+2} and H^{+} on an αFeOOH (geothite) to determine the degree to which these thermodynamic expectations are met.

47. THERMODYNAMICS AND KINETICS OF GAS-LIQUID METAL REACTIONS AND OF REACTIVE METAL-SOLVENT METAL REDUCTION REACTIONS

N. A. D. Parlee, Professor of Metallurgy, Applied Earth Sciences

Active Advisors:

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*Completed Ph.D. during report period.

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Argonne National Laboratory (ERDA)

Technical Objective:

To study the equilibria and rates of important gas-liquid metal reactions and interactions in order to elucidate the thermodynamics and kinetic mechanisms involved, and to relate these to the improvement of industrial materials and processes. To study the carbothermic and carbonitrothermic reduction of reactive metal oxides (e.g. UO_2, TiO_2, ZrO_2) in liquid metal solvents and the recovery of the reactive metals.

Approach:

Determination of thermodynamic and kinetic relations from equilibrated and dynamic systems of gases and liquid metals. The gases mainly include H_2, O_2, and N_2 but low boiling metal species such as Ca and Mg have received considerable attention although no new work on them is reported this year. Laboratory determination of the equilibria and rates of carbothermic and carbo-nitrothermic reduction of various reactive metal oxides in liquid solvents (e.g. Sn, Cu) and study of the various methods of recovery of the reactive metals from the alloys.

Research Report:

(1) The Absorption, Evolution and Diffusion of Gases in Liquid Metals

Graduate Student: E. Auza

The removal of gases (hydrogen, oxygen and nitrogen) from liquid metals before they are cast is extremely important because the physical properties of the solid product are often limited by the content of these gases, even after the best working and heat treatment. Rates of gas absorption and removal, and the factors controlling them, are being studied. Since these rates are often controlled by gas diffusivities in the metal a large part of the research has involved measurement of diffusivities in liquid metals and alloys, and developing methods of D_{gas} prediction -- which will be valuable in the design and improvement of processes. The research findings and present program are described as follows: (1) Rates of absorption and effusion of gases have been measured in various stagnant and stirred liquid metals and alloys. These rates are often found to be controlled by the diffusion of the gas in the liquid metal[15,16,17]; an example of an exception is when a surface active element is present[17] in sufficient concentration to make a surface reaction rate controlling. (2) New "steady state"[15] and "unsteady state"[15,16,17,18] methods for the measurement of D_{gas} values in stagnant metal have been developed, leading to the first successful measurements of gas diffusivities in liquid metals ever made; also a new direct solid electrolytic cell - steady state method for D_{oxygen} has been developed and published. (3) Solubilities and interaction parameters are measured where such data are needed for calculating D values. (4) D_H, D_N and D_O values have been measured in important metals and alloys and Arrhenius equations developed, e.g., D_O in Ag[18] and Ag alloys, D_O in Cu and Cu alloys[19], D_H and D_N in Fe and many Fe-X alloys[16,17]. (5) The work on hydrogen in liquid Fe, Ni, Cu, Ag and Sn[15] demonstrated that rates of absorption and effusion of hydrogen were controlled by D_H in the metals. A rough linear correlation between log D_H and log S_H (gas solubility) was found which appears to be useful in predicting D_H in uninvestigated metals[15]. High S_H is associated with low D_H and Q_H and vice versa. (6) The work on D_H in Fe-X alloys[16] (where X is Mn, Cr, V, Nb, Mo, W, Ni, Co, Cu) has led to new methods of predicting D_H in Fe-X alloys, i.e. linear relationships exist between interaction parameter $\varepsilon_H^{(X)}$ and log D_H at any fixed concentration of X, for each period in which X occurs in the periodic table, also linear relationships are found to exist between log D_H and hydrogen solubility for any fixed X concentration for each period in the periodic table. (7) The work in D_N in Fe-X alloys[17] (where X is Al, Si, Ni, W, Sn, Co, Cr, Mo, V, Nb) has shown that rates of absorption and effusion of nitrogen are controlled by D_N in the liquid when the (surface active) oxygen content is below 0.02% (above 0.02% oxygen surface reaction controls, and at 0.05% oxygen absorption and effusion practically cease -- which explains the slowness of nitrogen removal from liquid steel by vacuum in certain types of industrial processes and suggests how to alter the processes to get it out). The work on Fe-X alloys has demonstrated that D_N can be predicted[17] from the linear relationships found (a) between log D_N and e_N^X, and (b) between log D_N and nitrogen solubility, both with respect to the individual periods in the periodic table in which alloying element X lies. Some elements such as Si increase D_N spectacularly, while others such as V and Nb have important depressing effects on D_N. (7) D_N values in pure Fe, Co and Ni are also inversely related[3] to nitrogen solubility. High gas solubility means that the metal atoms in the liquid have on the average a high affinity for the diffusing gas atoms, and thus the movement of gas atoms can be expected to be slowed in in their movement through the liquid. (8) Experimental work is proceeding along the following lines (a) the study of hydrogen and nitrogen diffusion in more complex alloys with the expectancy of extending the D_{gas} prediction methods to commercial alloys and alloy steels and (b) to check further the effects of surface active elements such as O and S.

(2) The Calculation of Diffusion Coefficients and Other Transport Properties in Liquid Metals from Atomic Properties

Graduate Student: P. Protopapas

Consultants: Professor Hans C. Andersen and Dr. B. J. Alder

If the diffusion coefficients and other transport properties needed for the design of new processes could be calculated, rather than measured experimentally, enormous sums of money could be saved. We have had remarkable success in the application of a new method to the calculation of diffusivities in several kinds of systems and extremely promising success with viscosities. This has come about by the close interaction of Mr. Protopapas with Professor H. C. Andersen of our Chemistry Department and various other professionals. The main vehicle of our transport studies is the Enskog theory of dense fluids, brought up to date through pair-correlation functions "at contact" obtained from the combined use of Percus-Yevick equations and the Carnahan-Starling equations of state. The most important missing information, for the application of the Enskog theory in liquid metals, is the knowledge of hard-sphere diameters of the liquid metals at different temperatures. This information may now be readily obtained through our newly developed method for calculation of hard-sphere diameters as a function of temperature, described in papers now published[5,6]. The progress to date is best illustrated by listing the titles of the following papers which have all either been published [5,6] or presented at national or international conferences[3,4,6,9,10]. (1) "On a Theory for Derivation of Hard-Sphere Diameters of Liquid Metals as a Function of Temperature"[6], (2) "A Theory of Transport of Liquid Metals. I. Calculation of Self-Diffusion Coefficients"[5], (3) "A Theory of Transport of Liquid Metals. II. Calculation of Metal-Metal, Metal-Alloy, Gas-Metal and Gas-Alloy Inter-Diffusion Coefficients"[3,9], (4) "A Theory of Transport of Liquid Metals. III. Calculation of Viscosity Coefficients"[10]. The method of calculating self-diffusion coefficients appears to be clearly superior to any other method when compared with experimental values. The method for metal-metal diffusivities shows very good agreement with experimental values.

The viscosity calculations show striking agreement with experiment. The results of calculation of gas diffusivities in liquid metals and alloys show good promise, and the thrust of the recent work is to refine, extend and assess the methods of calculating gas diffusivities in liquid metals and alloys. It is also hoped to extend the viscosity work to alloys more complex than binaries, where the method is already successful. It is believed that these general methods can probably be extended in the future to the calculation of diffusivities in complex alloys and to the calculation of various transport and equilibrium properties such as thermal conductivities, surface tensions, also perhaps to diffusivities in fused salts and slags. Organizations such as the A.E.C. laboratories are keenly interested in these possible applications.

(3) Nitrogen-Nitride Reactions in Liquid Uranium Alloys and Their Applications to the Reprocessing of Nuclear Reactor Fuels

Associate Director: Professor R. N. Anderson

Graduate Student: Kenneth Au

The thermodynamics and kinetics of precipitation reactions like $\underline{M} + 1/2\ N_2(g) = MN(s)$ are being studied where $\underline{M}$ is uranium or a fission product element dissolved in a liquid metallic solvent such as Sn, Cu, etc. It has been found here that when simulated spent uranium reactor fuel containing its usual concentration of fission products is dissolved in liquid tin and nitrided at nitrogen pressures $\not>1$ atm the UN precipitates and sinks to the bottom leaving the fission products behind in solution. The solution containing its fission products can be separated from the purified UN; this UN can be redissolved in pure solvent by vacuum denitrification to give a pure U-Sn alloy from which the purified U can be recovered by various well known methods.

This offers (a) a new method of reprocessing reactor fuels, which appears to be less time consuming and ecologically superior, (b) a method of separating Zr fuel cladding, because ZrN floats, (c) a new method of making UN, a superior reactor fuel, (d) the concept of a completely new type of power reactor, where dangerous supercriticality is automatically avoided by decomposition of the nitride with rising temperature and re-solution of the uranium in the silute solvent, (e) the possibility of in-situ reprocessing of the fuel via recycling the metallic solution thru graphite tubes and containers, which are not attacked. (f) The recovery of waste fission products "locked up" in an unleachable metal alloy block. (g) New methods of separating Zr and Hf, of separating Zr from used nuclear cladding, and U, Nb and Zr from "mulberry" nuclear plant waste.

Progress is as follows: (1) The thermodynamics of the uranium nitride formation and decomposition reactions in liquid Sn have been fully elucidated[20]. (a) The thermodynamics of the nitride formation and decomposition reactions of certain representative fission products (in liquid Sn) such as Gd, Y and Pr have been fully elucidated[2,7,11,12,13,14] and others are being studied. (3) Nitrogen-nitride equilibria in U-Gd-Sn, U-Pr-Sn, U-Zr-Sn alloys have been studied[2,13,14] and the efficiency of the fission product separations by selective nitride precipitation has been demonstrated. (4) The kinetics of the UN formation and decomposition reactions in liquid tin solvent in induction stirred melts have been studied. For the formation reaction, a kinetic model and equation have been developed which explain the observed rate phenomena exceedingly well[1]; this model involves "mixed" rate control by (a) transport of dissolved nitrogen in the liquid U-Sn alloy and (b) chemical reaction between dissolved $\underline{N}$ and $\underline{U}$ in the stirred bulk. (5) The equilibria and thermodynamics of the uranium nitride formation and decomposition reactions in various other solvents (e.g. Cu, Pb, Ni) are being studied. (6) Separation of U from seven representative fission products in a synthetic spent reactor fuel has been demonstrated[14].

(4) Recovery of Zirconium from Zircalloy Cladding (Hulls) from Spent Nuclear Reactor Fuel Rods and Disposal of Clinging Nuclear Wastes

Co-directors - Professors Parlee and Anderson
Graduate Students - G. S. Selvaduray
J. R. Wang

At present there is no satisfactory way of recovering valuable pure Zr from the zircalloy "hulls" of spent nuclear fuel rods after the spent fuel is removed. These "hulls" are heavily contaminated with spent fuel and radioactive wastes. Waste handling and permanent disposal is also a problem.

The basic research is designed to test and develop the following scheme (a) dissolution of the "hulls" in liquid Sn or Cu, with a little added carbon to convert clinging oxides to dissolved metal (b) precipitation of the zirconium as ZrN by nitriding leaving all wastes behind in solution, ZrN floats, (c) recovery of Zr by decomposition of ZrN in a little new solvent metal to yield a Zr-Sn or Zr-Cu liquid alloy, followed by recovery of the Zr from the alloy by one of several means. This may be essentially simultaneous if the evaporation method is used, (c) concentration of the radioactive wastes in a Cu, Sn or Pb alloy ingot for easy handling and permanent disposal in the earth, in essentially unleachable form.

The present research is involved with

(1) The determination of the equilibria in the following all important reaction at various concentrations and temperatures (600°C to 1600°C)

$$\underline{Zr}\ (\text{dissolved}) + 1/2\ N_2\ (g) = ZrN\ (s)$$

Graphite or BeO crucibles do not contaminate the ZrN.

(2) The dissolution of zircalloy and simulated non-radioactive clinging wastes in Cu or Sn, nitriding to produce ZrN (which floats on the surface), and checking to confirm that all waste products are left behind in solution due to their much lower concentration and activity-reactivity - as is the case with uranium spent fuels.

(3) If (1) and (2) are successful further work will be on improved methods of Zr recovery from ZrN, and more work on disposal of

wastes which has already received some study in the case of uranium spent fuel wastes.

(5) Carbothermic and Carbo-Nitrothermic Reduction of Reactive Metal Oxides in Metal Solvents

Associate Director: Professor R. N. Anderson

Graduate Student: N. Bakshani

Production of reactive metals (Ti, U, Zr, B, Cb, Mg) is currently expensive because long complex procedures involving expensive reducing agents or expensive electricity are used. Usually the cheap reducing agent carbon cannot be used in conventional carbothermic reduction because the product is carbide or mainly carbide instead of metal. It has been discovered here that carbon can be used as the reducing agent if the reduction is carried out in or with a solvent metal (such as Sn or Cu), specially chosen to reduce the reactive metal's activity below the point where carbide can form. Two reaction schemes are involved. ($\underline{M}$ underlined represents the reactive metal dissolved).

Scheme (1) $MO_2(s) + 2C(s) = 2CO(g) + \underline{M}$ (dissolved)

Scheme (2) $MO_2(s) + 2C(s) + 1/2\ N_2(g) = MN(s) + 2CO(g)$

followed by $MN(s) = \underline{M} + 1/2\ N_2(g)$ in vacuum.

The reactive metal can be recovered from the alloy by one of several methods, such as distillation, metal solvent extraction, cooling to eutectic, withdrawing crystal rods, etc. This research is in its early stages but shows much promise. The UO_2 reduction works exceedingly well by both reaction schemes. U, Ti, Zr, Mg and Si have been produced. The TiO_2 reduction to the metal works best via the carbo-nitrothermic route. The nitride routes can produce very pure metal. Current work involves the measurement of equilibria in these reactions, observation of factors affecting the kinetics, methods of achieving 100% reduction, experiments on various methods of recovery of the reactive metal from the alloy, and study of the purity of the product metal.

Uranium is receiving the most attention at present, it not only represents a typical reactive metal for reduction, but fits into our present extensive research on (a) reprocessing methods for UO_2, UC and UN spent reactor fuels and (b) recovery of uranium in any desired purified fuel form i.e. U, UO_2, UN and UC.

Additional exploratory work is proceeding simultaneously on Ti, Zr, Mg, Si. Mg apparently can be made by two different methods via Scheme I, one involving simultaneous distillation. Electronic grade Si appears possible by a special method of separation from the alloy.

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48. ELECTRICAL, OPTICAL AND METALLURGICAL PROPERTIES OF SEMICONDUCTING MATERIAL

G. L. Pearson, Professor, Electrical Engineering

Professional Associates:

B. L. Mattes

Graduate Students:

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S. Y. Chiang*
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* Received Ph.D. during report period.
** Received M. S. during report period.

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Technical Objective:

To prepare new semiconducting materials, measure their pertinent properties, and construct novel devices therefrom.

Research Report:

(1) Properties of Vacancy Defects in GaAs Single Crystals

Graduate Student: S. Y. Chiang

Photoluminescence measurements made at various depths below the surface of annealed GaAs single crystals are compared with vacancy distribution profiles obtained from electrical measurements. Results on unodped n-GaAs indicate that isolated Ga or As vacancies form nonradiative centers. A broad band emission at 1.20 eV, arising from V_{Ga}-donor complexes, is observed in spectra taken from n-type samples doped with Si, Sn, or Te. The intensity of the 1.20 eV band varies with depth and reaches its maximum value in the region where Ga vacancies are dominant. These results show the consistency between photoluminescence and electrical measurements. A band at 1.37 eV has previously been assigned to V_{As}-acceptor complexes. This band was observed in the present study only when the samples had been annealed in ampoules prepared from quartz containing traces of Cu. It is concluded that the 1.37 eV band is due to Cu contamination rather than V_{As}-acceptor complexes.

(2) Fundamental Studies of $Al_xGa_{1-x}As$-GaAs Heterojunctions For Solar Energy Conversion

Graduate Student: D. T. Cheung

Properties of n($Al_xGa_{1-x}As$)-p(GaAs) heterojunctions grown by liquid phase epitaxial (LPE) techniques were investigated. It was found that an energy barrier in the form of a "spike" can be formed at the interface as a result of Zn out-diffusion from the GaAs layer. When Ge was substituted for Zn as the p-type dopant, no such energy barrier was observed. The results are interpreted in terms of the graded-gap heterojunction model.

(3) Preparation and Properties of $Al_xGa_{1-x}Sb$

Graduate Student: K. Y. Cheng

The ternary liquidus-solidus Al-Ga-Sb phase diagram in the Ga-rich region has been established. Liquidus isotherms at 400, 450, 500, and 500°C were determined by use of a weight-loss technique. Solidus isotherms were determined on undoped epitaxial layers of $Al_xGa_{1-x}Sb$ single crystals grown on (111) GaSb substrates from Ga-rich melts. A vertical liquid phase epitaxial (LPE) system was used. The growth temperatures were 500 and 550°C, and compositions ranging from 4 through 92% AlSb were obtained. A calculated phase diagram in the Ga-rich region, which is in excellent agreement with these experimental data, has been obtained. The calculations are based on a simple solution model for the ternary liquid and assume that the mixed crystals form an ideal solid solution. Band gap energy as a function of mixed crystal composition was measured at room temperature using optical absorption, wavelength modulated absorption, photoluminescence and electron microprobe techniques. Wavelength modulated absorption and photoluminescence measurements were also performed at 77°K. The maximum direct band gap energy at 300°K is 1.0 eV which corresponds to a mixed crystal composition of 24.5% AlSb. The infrared lattice vibration spectra have been studied in the Reststrahlen region. Two-mode behavior was observed in all alloy compositions. The optical absorption and wavelength modulation measurements were carried out at the Xerox Palo Alto Research Center.

(4) Grown Junction GaAs Solar Cell

Graduate Student: C. C. Shen

$P^+(Al_xGa_{1-x}As{:}Ge)$-$p(GaAs{:}Ge)$-$n^+(GaAs{:}Te)$ solar cells were fabricated using multiple layer liquid phase epitaxial (LPE) growth techniques. Germanium was used as the p-type dopant to eliminate impurity diffusion and to maximize minority carrier diffusion lengths. These procedures provide precise control of the thickness and carrier concentration of each individual layer.

A scanning electron microscope (AMR Model 900) was used extensively in the present work. Good delineation of grown layers was obtained by using the secondary emission mode, while the beam-induced current technique was adapted to evaluate minority carrier diffusion lengths as a function of free carrier concentration in LPE layers doped with Zn, Ge, Sn, Te, etc.

Solar cell conversion efficiencies in excess of 11% were obtained. By optimizing the cell parameters and further improving the fabrication processes (including the contact grid and the antireflection coating) we expect to achieve ≈20% efficiency in the near future.

(5) Growth and Properties of Semi-Insulating Epitaxial GaAs

Research Associate: B. L. Mattes

Graduate Student: Y. M. Houng

We have found that in order to grow liquid-phase epitaxial (LPE) semi-insulating GaAs layers, Cr must be used to form deep energy levels, and the shallow donors and acceptors must be self-compensated. The shallow and deep levels appear to be dependent on impurities that arise from chemical reactions between the growth system components. The reactions can be controlled by systematic bakeouts of the As-saturated Ga melt before each growth. This effect has been dramatically demonstrated in layers grown from melts baked out in the temperature range from 600° to 850°C. For example, layers grown from melts baked out below and above ~775°C in a fused quartz-graphite-hydrogen growth system change from n- to p-type, respectively. The bakeout transition temperature is essentially independent of the growth temperature and the Cr concentration. The resistivity in layers grown from undoped melts increases smoothly through the transition range. However, the resistivity reaches a peak of ~10,000 Ω-cm in layers grown from Cr-doped melts baked out at the transition temperature. Electrical and mass spectrographic measurements on layers grown from undoped and Cr-doped melts indicate that electrical and chemical compensation occurs between impurities in the melt and in the layer. Photoluminescence measurements at 77°K show 1.3 and 0.8 eV emission bands for n- and p-type layers grown from Cr-doped melts, respectively. In the high-resistivity layers, many unidentified deep levels are observed from 0.6 to 1.2 eV that parallel levels found in a Cr-doped, semi-insulating GaAs substrate.

(6) Fundamental Studies of AlGaAs-GaAs n-n Heterojunctions with Applications to Au-AlGaAs-GaAs Schottky Barrier Solar Cells

Graduate Student: Y. D. Shen

It has been conceived that, if a solar cell is fabricated by forming a transparent Schottky barrier on an AlGaAs-GaAs n-n heterojunction, it will have a much higher efficiency than ordinary p-n junction or Schottky barrier solar cells. This is due to expected increases in output voltage without concomitant losses in current output. Successful operation of the composite Schottky barrier solar cell, however, depends critically on a basic understanding of the properties of the AlGaAs-GaAs n-n heterojunction.

We have grown large area n-type $Al_xGa_{1-x}As$ and GaAs layers on heavily doped n^+GaAs substrates by means of liquid phase epitaxy. The layers (on the average) have usable areas in excess of 1 x 1 cm. One 1.5 x 2 cm double layer sample was grown. The thicknesses of the GaAs layers are on the order of 5 μm, and the $Al_xGa_{1-x}As$ layers on the order of 1 μm. Both layers are n-type and in the doping range of $n = 10^{16}$ cm^{-3}. The values of x in the $Al_xGa_{1-x}As$ layers are between 0.3 and 0.45. Suitable procedures for making satisfactory Schottky barriers on $Al_xGa_{1-x}As$ are under investigation.

The energy band diagrams of $n(Al_xGa_{1-x}As)$-n(GaAs) heterojunctions are being studied in detail in order to predict the characteristics of $Al_xGa_{1-x}As$-GaAs Schottky barrier solar cells and aid in the design of cells having maximum efficiencies.

(7) Lattice Defects in Annealed GaAs and $Al_xGa_{1-x}As$ Single Crystals

Graduate Student: K. I. Chang

We are extending our work on GaAs to other III-V binary and ternary compound semiconductors. In particular, we are investigating vacancy defects and vacancy-impurity complexes in the $Al_xGa_{1-x}As$ system at various values of x. Previous work has shown that Ga vacancies are acceptors and As vacancies are donors in GaAs. We have as yet been unable to determine the energy levels associated with either type of vacancy since both are non-radiative and therefore produce no detectable photoluminescent spectra. Our present attempt to solve this dilemma is to grow a thin layer of the material under investigation on a semi-insulating GaAs substrate, produce defects in the layer by annealing, prepare a Van der Pauw sample and make Hall measurements at elevated temperatures. Preliminary results on GaAs are encouraging and we plan to extend this technique to thin layers of $Al_xGa_{1-x}As$.

(8) A Study of Defects in GaAs Single Crystals Using Thermally Stimulated Capacitance Techniques

Graduate Student: J. S. Kim

The purpose of this study is to determine the trapping densities and activation energy levels of Ga and As vacancies near the surface of annealed GaAs single crystals. The thermally stimulated capacitance technique is concerned with changes in the charge states of traps which exist in the depletion layer of p-n junctions or Schottky barriers.

Undoped n-type wafers having a carrier concentration of 1.2×10^{16} cm^{-3} were annealed at 800°C for 24 hours in an evacuated Spectrosil ampoule. Gold Schottky barriers were made on both annealed and unannealed wafers for comparison purposes.

A Si temperature-sensing diode, which provides a dynamic temperature read-out signal, was constructed and calibrated (V_F vs T) at a constant forward current $I_F = 10\ \mu A$.

The diode was placed in thermal contact with the Schottky barrier under test and inserted in a light tight cryogenic dewar. While the temperature was raised from liquid nitrogen to ambient using various heating rates β_m (0.2 - 1.0°K/sec), barrier capacitance versus forward voltage curves (C vs V_F) were plotted on an X-Y recorder. From shifts in the capacitance curves at fixed values of β_m and $\ell n(T_m^4/\beta_m)$ vs $1/T_m$ plots one can evaluate the trap densities as well as their activation energy levels. T_m is the temperature at which dc/dT is a maximum. The activation energies obtained by this technique will be compared with those derived from Hall measurements at elevated temperatures.

PUBLICATIONS

1. "Velocity Saturation in n-type $Al_xGa_{1-x}As$ Single Crystals," A. A. Immorlica and G. L. Pearson, Appl. Phys. Letters 25, 570 (1974).
2. "Evidence of Two Channel Excitation of Luminescence in CdF_2:Mn," J. M. Langer, T. Langer, G. L. Pearson and B. Krukowska-Fulde, Phys. Stat. Sol. (a) 25, K61 (1974).
3. "Shallow Donor States in Semiconductor CdF_2," J. M. Langer, T. Langer, G. L. Pearson, B. Krukowska-Fulde and V. Piekara, Phys. Stat. Sol. (b) 66, 537 (1974).
4. "A Simplified Model for Graded-Gap Heterojunctions," D. T. Cheung, S. Y. Chiang and G. L. Pearson, Solid-State Electronics 18, 263 (1975).
5. "An Analysis of the Superinjection Phenomenon in Heterostructure Devices," D. T. Cheung and G. L. Pearson, J. Appl. Phys. 46, 2313 (1975).
6. "Crystal Growth, Phase Diagram and Band Gap Evaluation of $Al_xGa_{1-x}Sb$," K. Y. Cheng and G. L. Pearson, Bull. Am. Phys. Soc. 20, 29 (1975).
7. "A Study of the Optic Phonons in $Al_xGa_{1-x}Sb$," G. Lucovsky, K. Y. Cheng and G. L. Pearson, Bull. Am. Phys. Soc. 20, 29 (1975).

49. SCATTERING OF RADIATION BY LIQUIDS AND POLYMERS

R. Pecora, Associate Professor, Chemistry

Professional Associates:

Charles W. Beer, Jr.

Graduate Students:

S. R. Aragon
D. R. Bauer
C. W. Cornelius
K. J. Czworniak*
L. P. Miller

*Received Ph.D. during report period

Agency Support:

NSF-GP-38228X1
NSF through CMR

Technical Objective:

The formulation of theories of the scattering of radiation from liquids and polymer systems in relation to their structure and thermal motions. The experimental study of fluid and polymer structure and dynamics by light scattering spectroscopy.

Approach:

Radiation scattering theories are formulated in terms of fluid space-time correlation functions. Theories of liquid dynamics and structure are then constructed in terms of relevant structure and transport parameters.

Experimental studies are carried out over the whole frequency range accessible to light scattering spectroscopy

($10 \approx 10^{14}$ Hz).

Research Report:

(1) Development of a Light Scattering Label Technique
Graduate Student: D. R. Bauer

Depolarized light scattering has been shown to be a useful probe of the dynamics of molecular reorientation in liquids. There are, however, several difficulties with this technique. One is that since depolarized scattering is relatively low in intensity it is difficult to study solutes in dilute solution. Another is that depolarized light scattering is not selective in that in a complex mixture many of the components have comparable depolarized intensities thus masking the scattering from a particular component. A technique which enhances the scattering from a given species would be very valuable in probing complex mixtures or dilute solutions. Such strongly scattering species could be used as light scattering labels.

We have investigated the scattering from a series of diphenylpolyenes using light wavelengths near the molecular absorption wavelengths and have found a strong resonance enhancement of the intensities of the depolarized scattering. Furthermore, this absorption does not affect the spectra of the scattered light. Thus, the rotational motions of these substances can be studied down to very low concentrations ($\sim 10^{-4}$ molar).

These experiments have been done in CCl_4 solution. In the coming year we plan to introduce these molecules into media such as vesicles and membranes and then from depolarized Rayleigh spectroscopy measurements to study rotational motion of the diphenylpolyenes in these media.

(2) Studies of Phospholipid Vesicles

Graduate Student: S. R. Aragon

Light scattering studies of the size, shape and rate of growth of aqueous dispersions of phospholipid vesicles have been conducted in the past year and will continue.

In the past year we have developed techniques for studying the distribution of sizes of phospholipid vesicle dispersions using dynamic isotropic Rayleigh scattering measurements. These methods allow us to determine both "average" sizes and the distribution of sizes and changes in these quantities.

(3) Light Scattering from Macromolecules

Graduate Students: D. R. Bauer
L. P. Miller

(A) Studies of rotational motion of several protein molecules in solution have been performed by depolarized light scattering. In particular, we have found the rotational correlation time of muscle calcium binding protein (MW = 12,000).(2) We have also obtained carbon 13 nuclear relaxation data on the alpha carbons in this molecule and found that the correlation time for these carbons is the same as that obtained from light scattering for the overall molecular motion. Thus, we concluded that the alpha carbons in this molecule form a rigid backbone which rotates with the molecule.

(B) Depolarized Rayleigh scattering studies on narrow fraction polystyrene solutions as a function of molecular weight have been carried out.(3) It is found that the depolarized spectra each exhibit two relaxation times: one proportional to the polymer molecular weight and the other independent of molecular weight. The relaxation time proportional to the molecular weight has been assigned to an intramolecular motion which involves moving a large part of the macromolecule. The faster, molecular weight independent time represents a local motion of the chain, which we believe to be "correlated" motion of phenyl groups around the main chain axis. We have also formulated a simple Mori type theory for this correlated motion.

(4) Mutual Diffusion Coefficients of Binary Liquid Solutions
Graduate Student: K. J. Czworniak

A theoretical and experimental study of diffusion coefficients of binary liquid solutions has been completed. Dynamic light scattering was used to measure the diffusion coefficients for many mixtures over a wide composition and temperature range. A simple "hard sphere" theory can be used to explain the results for most of the liquids studied.

(5) Fluorescence Correlation Spectroscopy
Graduate Student: S. R. Aragon

A theory relating rotational Brownian motion to the time autocorrelation function of the intensity of radiation from a fluorescent system composed of spherical rotors has been formulated.(4) It is hoped that fluorescence fluctuation spectroscopy can be used to complement light scattering in measuring rotational correlation times of molecules.

(6) Studies of Molecular Complexes

Postdoctoral Associate: C. W. Beer

A study of complexes of CBr_4 and the xylenes has been performed using depolarized Rayleigh scattering.

Reference Publications:

1. "Theory of Dynamic Light Scattering from Polydisperse Systems" by S. R. Aragon and R. Pecora, J. Chem. Phys., in press.
2. "Depolarized Light Scattering and Carbon Nuclear Resonance Measurements of the Isotropic Rotational Correlation Time of Muscle Calcium Binding Protein" by D. R. Bauer, S. J. Opella, D. J. Nelson and R. Pecora, J. Am. Chem. Soc. 97, 2580 (1975).
3. "Depolarized Rayleigh Spectroscopy Studies of Relaxation Processes of Polystyrenes in Solution" by D. R. Bauer, J. I. Brauman and R. Pecora, Macromolecules, in press.
4. "Fluorescence Correlation Spectroscopy and Brownian Rotational Diffusion" by S. R. Aragon and R. Pecora, Biopolymers 14, 119 (1975).

50. PHASE TRANSITION KINETICS

G. M. Pound, Professor, Materials Science and Engineering

Graduate Students:

B. A. Chin
J. Miyazaki
M. Mruzik
M. Thomas

Agency Support:

NASA-NCAR 745-405
NSF GH-41523
NSF through CMR

Technical Objective:

To gain a better understanding of the physics of phase transformations and other thermally activated rate processes of interest in materials science, metallurgy, mechanical engineering, and meteorology.

Approach:

Theoretical and experimental investigations of homogeneous nucleation in condensation from the vapor and freezing of liquids, of heterogeneous nucleation on substrates and of other thermally activated rate processes.

(1) Statistical Mechanical Calculation of Surface Tension and Structure in a Liquid-Vapor Interface (Argon)

(with Mr. Jun Miyazaki, graduate student, and Dr. John Barker)

In order to compare our results for the "exact" free energies of clusters with the capillarity approximation, the surface tension of bulk liquid argon was calculated by both Monte Carlo and perturbation methods. In the Monte Carlo method the usual periodic boundary conditions were imposed with respect to translations parallel to the free surfaces, and an external potential was used to prevent indefinite evaporation of molecules in the finite system. For the same L-J 12-6 potential used in the cluster calculations and a 468 atom system, the surface tension at 84°K was found to be 16.64 ± 2.62 ergs/cm^2. However the surface tension by this Monte Carlo method does fluctuate, as evidenced by the rather large precision measure of ± 2.62 dynes/cm. Accordingly, a more accurate calculation was made by using the Monte Carlo method to estimate directly the free energy and energy required to create the surface rather than to make an infinitesimal change in surface area, as in the previous calculation. A value of 18.34 ± 0.28 ergs/cm^2 at 84°K was obtained.

(2) The Structure and Specific Free Energy of the Liquid-Crystal Interface of Argon

(with Mr. Jun Miyazaki, graduate student, and Dr. John Barker)

It is proposed to use the same Monte Carlo Method described above to calculate the structure and specific free energy of the liquid-crystal interface of argon at the melting point. The same L-J 12-6 potential will be used, and the only difference in the calculation will be that the mean orientation of the liquid-crystal interface will be constrained, e.g., to the (111) orientation. This is an easy constraint to apply in the present calculation. The calculation will then be repeated for other orientations. In this way a polar diagram of the liquid-crystal specific interfacial free energies will be constructed. Also, the structure, i.e., the density profile, will be obtained as a function of orientation as a result of the calculation. It is anticipated that some kind of periodic structure will be obtained in the liquid near the interface. Further, the crystal may show some interesting form of "interface roughness". All of this is of great interest, particularly in relation to the growth process in the freezing of liquids, a matter of some technological importance.

(3) Monte Carlo Study of Ion-Water Clusters

(with Mr. Mike Mruzik, graduate student, Dr. Donald E. Schreiber and Professor Farid F. Abraham).

The procedures developed in this work have been employed to calculate theoretical free energies of formation of ion-water clusters for comparison with experiment. Gibbs free energies were calculated for the gas phase reaction:

$$\text{ion}(H_2O)_{N-1} + H_2O_{(vapor)} = \text{ion}(H_2O)_N$$

for the Li^+, Na^+, K^+, Cl^-, and F^- ions and for N = 1 to 6. The standard state for all calculations was taken as 298°K and 1 atmosphere. The Monte Carlo method was used to evaluate the appropriate classical expressions of statistical mechanics by employing the intermolecular potential functions recently developed from ab initio Hartree-Fock calculations. Enthalpies, entropies, and structural information were also calculated. Agreement with experiment is sufficiently good to demonstrate the feasibility of this approach.

(4) Creep and Diffusion Coefficients in Solid Solutions
(with Mr. Bryan Chin, graduate student, Dr. Robert Stang, Dr. Vikram Rao, and Professor W. D. Nix)

In reexamining the diffusional creep process, some questions have arisen that offer the promise of exciting theoretical and technological developments. Sellars and Quarrell, in measuring creep rates in Au-Ni alloys, found anomalously high creep rates in alloys containing 66 atomic percent Ni at temperatures above the miscibility gap. This effect was reproduced consistently at all the stress levels and at two different temperatures. No explanation for this phenomenon had been forwarded to date until Rao and Nix, using a semi-empirical approach, reproduced the essential features of the behavior. This approach can be used to predict extraordinarily high creep rates in alloys under certain conditions of composition, temperature and pressure. This offers attractive possibilities from a fabrication point of view. Also, another deduction from the new approach is the prediction of sharp drops in creep activation energies of compounds such as UO_2 at off-stoichiometric compositions. This and related phenomena have important applications for the use of ceramic fuels in nuclear reactors, where the phenomenon has been noted and not satisfactorily explained.

In the course of the present work, a linked-flux analysis was applied to the problem of stress-assisted diffusion in solid solutions, exact results were obtained, and the qualitative form of Rao and Nix's empirical relationship was verified. Crudely speaking, the diffusion or creep rate is an inverse function of the thermodynamic factor.

However, also in the course of the present work, creep rates in aluminum-zinc alloys were measured at temperatures above the miscibility gap, and the theoretically predicted enhancement of creep rate was not found.

(5) Angstrom-Particle Catalysis

(with Mr. Mike Thomas, graduate student, and Professor Helmut Poppa)

Important examples of catalysis can be found in such areas as petroleum refining or automobile exhaust systems. Thus it is essential to evaluate and to predict a catalyst's performance, but at present there is no sound criterion for the design or evaluation of catalyst systems in terms of physical properties such as particle size and structure.

The catalyst being used in this experiment is Pd, which is vapor-deposited onto clean mica substrates in a vacuum on the order of 10^{-10} torr. Substrate temperatures and vapor deposition rates are varied in order to generate thin films of catalyst crystallites having various sizes and crystallographic structures. Particle sizes, morphology and crystal structures are determined using a high resolution TEM, TED, and electronic image analysis. The size distributions of the catalyst particles produced in various tests are evaluated from these data, using image computer techniques. The catalytic properties of the film will now be evaluated in-situ by localized reaction of a gaseous species, such as C_6H_6, on the catalyst surface in vacuum and analyzing the reaction products with a mass spectrometer. (The general type of chemical reactions studied will involve hydrogenolysis and a specific reaction will be selected which maximizes the influence of particle size (effects.) In this way, the catalysts' performance will be evaluated by determining the rate and extent of reaction. Any changes in the catalysts' particle size over varying ranges of temperature and reaction time will also be studied, along with the possibility of selecting materials which will minimize "Ostwald Ripening" of the catalyst under high reaction temperatures. This ripening effect often reduces the catalytic activity severely.

Reference Publications:

1. Yasuto Miyazawa and G. M. Pound, "Homogeneous Nucleation in Freezing of Gallium", J. Crystal Growth 23, 45 (1974).

2. Kazumi Nishioka and G. M. Pound, "Homogeneous Nucleation in Vapors", a chapter in "Surface and Colloid Science", Vol. 8, edited by Egon Matijevic, John Wiley, New York (1975).

3. K. Nishioka and G. M. Pound, "Theory of the Replacement Partition Function for Crystals in Homogeneous Nucleation", Acta Met. 22, 1015 (1974).

4. K. Nishioka and G. M. Pound, "Theory of the Replacement Partition Function for Crystals in Homogeneous Nucleation", J. Crystal Growth 24/25, 511 (1974).

5. G. M. Pound, "Selected Values of Critical Supersaturation for Nucleation from the Vapor of Crystals on Substrates", "Preparation and Properties of Solid State Materials" (in press).

6. Kazumi Nishioka and G. M. Pound, "Statistical Mechanics of Homogeneous Nucleation in Vapor", a chapter in "Nucleation", Volume II, edited by A. C. Zettlemoyer, Dekker, New York (in press).

7. Eal Lee, Helmut Poppa and G. M. Pound, "Quantitative Measurements of Nucleation and Growth Kinetics of Gold on Mica", J. Crystal Growth (submitted).

51. MICROWAVE ELECTRONICS

C. F. Quate, Professor, Applied Physics and Electrical Engineering

Graduate Students:

A. Albanese
T. W. Grudkowski*
R. A. Lemons*
N. J. Moll

*Received PhD during report period.

Agency Support:

Navy N00014-75-C-0632
Navy N00014-75-C-0359
Navy N00014-75-C-0778
AF F30602-74-C-0038
Army DAHC04-74-G-0093
Hartford Foundation
NSF ENG75-02028
NSF APR75-07317

Technical Objective:

In this program we are investigating the physical phenomena underlying the propagation and radiation of acoustic waves over a range of frequencies which extend into the microwave region. The ultimate goal is the realization of devices and composite systems which exploit this form of radiation for the purpose of processing and analyzing complex signals, scanning of images in the optical and infra-red region and in the construction of an acoustic microscope.

Research Report:

(1) Signal Processing and Imaging Using GaAs Nonlinear Acoustic Delay Lines

Graduate Student: T. W. Grudkowski

Signal processing applications, such as real time convolution, which arise from interactions between acoustic waves in a nonlinear delay line, have resulted in efforts to find techniques to perform these operations more effectively. The approach taken here involves the use of a piezoelectric semiconductor, GaAs. A monolithic structure has been developed, consisting of a reversed biased Schottky barrier diode fabricated on the surface of an epitaxial n/n^+ substrate. Efficient operation can be obtained with well oriented zinc oxide thin film transducers to launch the Rayleigh wave.

A novel monolithic Rayleigh wave convolver has been developed. Acoustic wave mixing occurs at the depletion edge of a reversed biased Schottky barrier diode electrode fabricated along the delay line surface. The efficiency of the interaction is found to be controlled by the amount of charge on the barrier electrode, with good agreement between experimental and predicted behavior. The uniformity of the structure results in near theoretical signal processing performance as demonstrated by the experimental autocorrelation characteristics achieved. Charge storage on the barrier electrode can be monitored in this type of interaction and on isolated barriers we have demonstrated storage times of several milliseconds.

Acoustic scanning of optical patterns using Rayleigh wave interaction within a Schottky diode array has been analyzed and the operation of an experimental device has been demonstrated.

(2) Mechanically Scanned Acoustic Microscope

Graduate Student: R. A. Lemons

The acoustic microscope - an instrument based on acoustic radiation at microwave frequencies - is designed for viewing the microscopic detail exhibited in the elastic properties of a given object. The most significant and the most recent improvement has been the introduction of mechanical scanning. With this innovation there has been substantial improvement in the resolving power since the new instrument has made it possible to work in liquid water with sound frequencies as high as 1000 MHz. The resolution in a carefully constructed instrument at this frequency approaches that of the optical instrument and it permits one to observe both the internal details of biological cells and the fine structure of integrated circuits. Even though the resolving power is not yet equal to the value that is achieved with optical waves it does bring into view an interesting part of the microscopic world and it should allow us to determine the ultimate utility of this form of the instrument.

(3) Thin Film Integrated Optics

Graduate Student: A. Albanese

In this research we are studying phenomena in optical guided waves. A basic goal in the research is the fabrication of good quality optical waveguides, passive devices, modulators and deflectors to be used in integrated optics.

Multimode and single mode optical waveguides have been made by out-diffusing Li atoms from $LiNbO_3$ in vacuum at 10^{-6} torr at 1100°C for a period varying between nine minutes and three hours. These waveguides are used to study acousto-optics, electro-optic and thermo-optic effects.

Light was successfully deflected in the plane of the guide with a surface acoustic wave (120 MHz, 250 mW) propagating perpendicular to the optical guided wave. Collinear interaction between light and surface acoustic wave was also achieved with the light being deflected out of the plane of the waveguide. A surface acoustic wave of 1 W, 120 MHz will convert 1% of guided light to unguided light and vice versa in one centimeter of interaction length.

Preferential chemical etching observed in $LiNbO_3$ was used to make asymmetric dielectric structures as blazed gratings and the "asymmetric coupler" for slab waveguides. The asymmetric coupler consist on a blazed grating with its grooves aligned parallel to the propagation of light. The spacing between two grooves is approximately 0.1 micron. The asymmetric shape of the groove efficiently couples the horizontal and the vertical polarization of the electric field at the boundary. A beam of ordinary light incident from the substrate is totally reflected in two beams of different polarizations. Due to the anisotropy of the substrate the two beams (ordinary and extraordinary light) travel at different angles. The angle of incidence can be adjusted such that the converted extraordinary light enters into the waveguide; and vice versa, an extraordinary guided wave can be converted to an ordinary wave as this wave will travel about 15° off the plane of the guide. In 1 cm of interaction length the measured conversion efficiency so far is 20%.

A new electro-optical light modulator and light multiplexer has been designed, built and tried experimentally. The electro-optical modulator consists of an optical waveguide made by metal diffusion into $LiNbO_3$ and two metal electrodes that produce an electric field normal to the propagation of the light. The electric field convert the incident wave (TE) into a wave of different polarization (TM). The light in the waveguide is coupled out by a prism coupler. The output beam leaves the prism at an angle depending on the polarization. The difference on the output angles between the TE and TM waves is 26°. For 5 mm of interaction length an electric field 1 volt/micron can switch 90% of the light from one beam into another beam.

Reference Publications:

1. T. W. Grudkowski and C. F. Quate, "Acoustic Readout of Charge Storage on GaAs", Appl. Phys. Letters, 25, 99-101 (15 July, 1974).

2. R. A. Lemons and C. F. Quate, "Integrated Circuits as Viewed with an Acoustic Microscope", Appl. Phys. Letters, 25, 251-253 (1 September 1974).

3. C. F. Quate, "Optical Image Scanning with Acoustic Surface Waves", IEEE Trans. Sonics & Ultrasonics, SU-21, 283-288 (October 1974).

4. R. A. Lemons and C. F. Quate, "Advances in Mechanically Scanned Acoustic Microscopy", 1974 Ultrasonics Symposium Proceedings, IEEE Cat. #74CHO896-1SU, 41-44 (November 1974).

5. T. W. Grudkowski and C. F. Quate, "Optical Image Scanning using Nonlinear Surface Wave Interaction in GaAs", 1974 Ultrasonics Symposium Proceedings, IEEE Cat. #74CHO896-1SU, 749-752 (November 1974).

6. R. A. Lemons and C. F. Quate, "Acoustic Microscopy: Biomedical Applications", Science, 188, 905-911 (30 May, 1975).

52. INVESTIGATION OF THE MICROMECHANICS OF EXPANSIVE REACTIONS IN CONCRETE AND DEVELOPMENT OF NEW EXPANSIVE CEMENTS

C. W. Richards, Professor, Civil Engineering

Professional Associate:

R. A. Helmuth

Graduate Students:

D. A. Burciaga

A. Kerdegari *

* Received MS during Report Period.

Agency Support:

NSF ENG 74-23775
NSF through CMR

Technical Objectives:

Completion of the micromechanical model developed during the previous year for free and restrained expansion of expansive cements and expansive concretes.

Development of methods of improving the performance and predictability of expansive cements based on conclusions drawn from the model.

Research Report:

Our research during the past two years had led to the development of a model for the expansive process which makes possible the identification of the important variables, and the calculation of free expansions in expansive cement pastes. An extension of the model to restrained expansion shows promise of providing equally useful information.

We propose a continuation of the research aimed at a) completion of the model for restrained expansion, b) further refinement of the model for free expansion, and testing on other types of expansive cements, and c) application of the theoretical analysis to concretes and mortars.

As a result of this research we expect to be able to recommend modifications of current practice in expansive cement manufacture for more predictable and reliable performance, both in "shrinkage compensating concrete" and in "self-stressing concrete." For self-stressing concrete we expect to be able to predict the maximum prestress that can be developed by a given cement, and optimize the design of the cement to produce maximum self-stressing for prestressed concrete members.

Current Research Program:

Work is proceeding along four lines:

1) Further experiments on free expansion of cement paste aimed at refinement of the model. Measurements of the progress of cement hydration are correlated with measurements of expansion, resonant frequency, weight gain, and compressive strength.

2) Measurements of free expansion of mortars to test that part of the model relating to the effects of aggregates on the progress of expansion.

3) Restrained expansion tests to determine the effects of changing the degree of restraint.

4) Experiments with expansive cements containing expansive components of variable chemical composition, particle size distribution, and quantity.

Reference Publication:

Expansive Cement Concrete: Micromechanical Models for Free and Restrained Expansion, Civil Engineering Technical Report No. 191, January 1975, by C. W. Richards and R. A. Helmuth.

53. PLATELET INTERACTIONS WITH BIOMATERIALS

C. R. Robertson, Associate Professor, Chemical Engineering

Graduate Students:

M. P. Bohrer
R. W. Bradshaw
H. N. Chang*
R. Chang*
G. L. Gussis
S. A. Moese
V. M. Sanjana*
L. R. Waterland*
R. Watkins

*Received Ph.D. during report period

Agency Support**

ACS-PRF 7295-AC4, 7
NIH-1R01-HL-14945
Engineering Foundation RC-A-73-5
Veterans Administration

Technical Objective:

To obtain an understanding of the manner in which hydrodynamic and biochemical factors influence blood platelet behavior in the initial events of thrombus formation.

Research Report:

(1) Platelet Adhesiveness

Graduate Student: H. N. Chang

Since platelet adhesiveness varies within mammalian species from one animal to another, a technique must be developed whereby these differences may be characterized prior to analyzing the formation of thromboses on foreign materials. With this information available, platelet-surface interactions may be correlated with hydrodynamic and surface properties exclusively, without having to contend with anomalies arising from unknown variations in blood chemistry in different experimental animals. Adhesion of rabbit platelets using citrated whole blood is being studied in columns

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**The research reported herein is presently unsupported. Activities supported by these agencies are in related areas.

containing clean glass beads. Data obtained from these experiments is being analyzed using a model of the unsteady--state behavior of a fixed bed absorber. Since this technique is very similar to that presently used by physicians, the results of this study will shed light on the primary factors which influence the operation of a glass bead column and thus provide physicians with a rational way to vary column parameters and experimental conditions when testing for platelet adhesiveness characteristic of diseased states. For example, the nature and amount of the anticoagulant used, the column diameter and height, blood residence time, and the size and composition of the glass beads all interact in a complex fashion to influence the overall observed platelet adhesiveness.

Once the technique has been developed and tested, it will serve as a preliminary screening method for determining the influence on platelet behavior of selected coatings placed on the glass beads. Also, we intend to develop a correlation between platelet response in the glass bead column (with or without coatings) and a specially developed laminar flow-cell which better represents the environment such as might be found in arterio-venous shunts, artificial organs, and extracorporeal circuits.

54. SPECTROSCOPY AND QUANTUM ELECTRONICS

A. L. Schawlow, Professor of Physics
T. W. Hänsch, Associate Professor of Physics

Professional Associates:

R. Bernstein, Visiting Scholar
P. Brooks, Visiting Scholar
R. Wallenstein, Visiting Scholar

Graduate Students:

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K. C. Harvey*
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C. E. Wieman

*Received Ph.D. during report period.

Agency Support:

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U.S. Navy ONR 71
USDC NBS4-9002-A1

Technical Objective:

To study the interaction between electromagnetic radiation and matter, to extend the range of coherent light techniques, to apply coherent and conventional light to elucidate problems in atomic, molecular and solid state physics.

Approach:

High resolution spectroscopy and fast-pulse electro-optical systems, using lasers where appropriate.

Research Report:

(1) Development of Monochromatic Tunable Dye Lasers

Graduate Students:	R. T. Hawkins
	C. Wieman
Visiting Scholar:	R. Wallenstein

A powerful, monochromatic pulsed dye laser oscillator-amplifier system has been developed. Peak powers of 50 kW in the visible at line widths down to 6.10^{-}[illegible] Å can be generated with a gas-pressure tuned dye laser oscillator with external filter interferometer, followed by a two-stage dye laser amplifier, pumped by one 1 MW nitrogen laser. Frequency doubling in lithium formate permits the generation of narrowband coherent UV radiation down to 2300Å. This laser system has already proven to be a powerful tool for high resolution laser spectroscopy of atoms and molecules.

Even narrower lines can be generated with several cw dye lasers available in our laboratories. Efforts are underway to extend the tuning range of these lasers by frequency doubling and sum frequency generation in nonlinear optical materials, and to improve their monochromaticity by active frequency looking to a resonant cavity or to a narrow atomic or molecular resonance line. We are also working at methods to improve the frequency calibration of tunable dye lasers, using interferometric and heterodyne techniques.

(2) Stark Effect in Excited Alkali Atoms, Observed by Doppler-Free Two-Photon Spectroscopy

Graduate Students: K. C. Harvey
R. T. Hawkins

The Stark splittings and shifts of the 4d and 5s levels of atomic sodium have been measured by the new method of Doppler-free two-photon spectroscopy, using a cw dye laser. The atoms in a short, sheet-like atomic beam with transverse external electric field are irradiated by two counter propagating laser beams, tuned to half the transition frequency, and the excitation is monitored by observing the UV fluorescence. The resonance lines are free of Doppler broadening, if one photon is absorbed from each beam, because from any atom moving in any direction the two waves have equal and opposite Doppler shifts so that their sum frequency is constant. The Stark effect of the 4d state is primarily due to a mixing with the neighboring 4f and 5p states. By measuring tensor and scalar polarizability separately, it has been possible to determine the oscillator strength of the transtion 4d-4f and 4d-5p without any need of knowing level population densities.

(3) Doppler-Free Two-Photon Spectroscopy of Hydrogen 1S-2S

Graduate Students: S. A. Lee
C. Wieman

Visiting Scholar: R. Wallenstein

We have observed transitions from the 1S ground state of atomic hydrogen and deuterium to the metastable 2S state by the method of Doppler-free two-photon spectroscopy, outlined in the preceeding section. The atoms are excited by absorption of two photons of wavelength 2430Å, provided by a frequency doubled pulsed dye laser, and the excitation is monitored by observing the subsequent collision-induced 2p-1s fluorescence at the L_α wavelength 1215Å. The fundamental dye laser wavelength at resonance, 4860Å, coincides with the visible Balmer-β line, and simultaneous recording of the absorption spectrum of this line permits a precise compensation of the energy intervals 1S-2S and 2S,P-4S,P,D. From such a comparison we have, for the first time, experimentally determined the Lamb-shift of the 1S ground state with an accuracy better than 1%.

We are presently working at further improvements of this accuracy, and we are also attempting accurate measurements of the 1S-2S isotope shift and absolute transition energy. Such measurements do not only provide new stringent tests of QED calculation, but they will also permit new precise determinations of important fundamental constants, such as the Rydberg constant or the ratio of electron mass to proton or deuteron mass.

(4) Cooling of Gases by Laser Radiation

It has been shown that a low density gas can be cooled by illuminating it with intense quasi-monochromatic light confined to the lower half of the resonance line's Doppler width. Translational kinetic energy can be transferred from the gas to the scattered light, until the atomic velocity is reduced by the ratio of the Doppler width of the natural linewidth. It is estimated that 1 cm^3 Mg vapor could be cooled from a temperature of 500 K to 0.24K in a time of 30 μsec by irradiating it with 0.1 J of laser light near the resonance wavelength 2852.1Å.

Reference Publications:

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8. T. W. Hänsch and A. L. Schawlow, Cooling of Gases by Laser Radiation, Opt. Comm. 13, 68 (1975).

55. INTERACTIONS OF ACOUSTIC RADIATION WITH SOLIDS

H. J. Shaw, Adjunct Professor and Associate Director,
Microwave Laboratory

Professional Associates:

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Navy	N00014-75-C-0778
Navy	N00123-72-C-0866
AF	RI74-20773

Research Report:

We have made further progress during the past year on obtaining long time delays with surface acoustic wave delay lines. The basic delay line uses helical wrap-around propagation to build up long time delays. In the past we have reported very long delays, reaching the multimilliseconds. During the past year we have been concerned with increasing the bandwidth of such delay lines, to achieve large bandwidth together with long time delay. The problem of the broadbanding of delay lines is different when long delay is involved, from those of conventional delay lines of shorter delay. We have demonstrated a delay line which operates at a center frequency of 83 MHz with time delay of

1 millisecond and bandwidth of 60 MHz, appropriate for the storage of some 6 X 10^4 bits of analog data at a data rate of 60 MHz.

Surface acoustic wave delay lines, in addition to their ability to provide time delay or storage, are also very well suited to doing rather arbitrary signal processing of the signals which they store. This can be accomplished directly on the delay line surface, in monolithic format. An example of such processing is the process of taking the Fourier transform of arbitrary signals. The new delay lines of large time-bandwidth product are viewed as vehicles for extending the range of such signal processing, and investigation of these possibilities is now being undertaken. This has potential for performing real time Fourier transforms and other transformations in the future, at speeds and data rates not accessible by other methods.

An acoustic scanning system suitable for non-destructive testing of materials and bio-medical applications has been constructed. This is a one-dimensional scanning system using an 85 element PZT array, producing bulk acoustic waves in water at 2.25 MHz, which are electronically scanned and focused with electronically variable focal length. Chirp signals for scanning and focusing of the array are obtained from a tapped surface acoustic wave delay line operating at 50 MHz. This machine has been in use for the past six months for the scanning of samples of industrial samples. Planar laminate samples of boron fibers bonded to titanium plates, supplied by North American Rockwell, have been studied. These samples contain intentionally debonded regions, which can be detected during scanning. Plates having face dimensions of 4" X 12" can be scanned in a single pass at real time TV rates, with transverse resolution of the order of 1 mm. Present activities are directed at improving the design of acoustic illuminators to improve their uniformity and reduce image artifacts. Real time scanners of this type promise very substantial reduction in the time and cost of area scanning of structural materials and parts.

A new type of acoustic scanning device has been devised which provides a simple means of focusing and scanning a beam of acoustic waves. An acoustic wave is scattered off of an array of parallel grooves which are fabricated on the surface of a solid block. By properly "coding" the original acoustic wave before it strikes the grating, the acoustic waves scattered by the grating are brought to a focus at some desired distance from the grating, producing a focused acoustic beam. This beam, furthermore, automatically scans along a line, and is in turn scattered from small objects or structures located within the solid, or within an adjacent liquid, leading to the imaging of these objects.

This system, termed a grating acoustic scanner, is a member of a class of acoustic scanning systems which can scan objects at high speed, and can thus be used to view moving objects. Alternatively, in scanning objects of large area, they can cover the area in a greatly reduced time, which is currently a very important issue in commercial nondestructive testing of materials. While this device is in a very preliminary stage, prototype models operating at a center frequency of 1 MHz have been successful in proving the principle, producing focused and scanned acoustic beams in aluminum solid blocks, whose characteristics agree with theoretical predictions.

The new system, in which the heart of the device is a simple array of grooves which form an acoustic grating, is unique, because it has the direct potential for working with acoustic waves of much smaller wavelength than other types of high-speed scanners. This means that it has the potential for viewing these objects with more precision and with higher detail.

A new type of analog-to-digital converter using a surface acoustic wave delay line has been devised. It uses a linear interaction mechanism, involving a basic property of surface acoustic wave transducers which has not heretofore been applied. It operates by comparing a reference signal, having a linearly varying amplitude versus time, with the analog input signal whose amplitude is to be digitized. The present device differs from standard integrating-type A/D converters in that the reference signal is produced by passing an rf tone pulse through an interdigital surface acoustic wave transducer which, because of its basic convolution property, produces an accurate linearly varying ramp. This process offers a potential advantage in terms of temperature stability. An integrated circuit comparator is used to relate the amplitude of a sampled analog bit from the analog signal to the ramp amplitude, and an integrated circuit counter then outputs the corresponding digital count. A first experimental model of this device has been demonstrated, using uniform interdigital transducers having 16 split-electrode finger pairs and operating with four-bit words, to prove the principle of the device.

A project has been initiated to study the acoustic propagation properties of thin sheets of Poly Vinylidene Fluoride (PVF_2). This is a polymer similar to the familiar Poly Vinyl Cloride (PVC) plastic which is widely used for industrial and household purposes, which can be rendered piezoelectric by suitable processing. PVF_2 is a ferroelectric material, and it was shown a few years ago in Japan that it can be made piezoelectric by a suitable poling operation. Recently workers in Germany showed that the piezoelectric property of PVF_2 films retains its effectiveness at frequencies up to 500 MHz. We thus have the rather exciting circumstance of a cheap plastic material which can be readily obtained in thin sheets of virtually arbitrary size, and which can be rendered permanently piezoelectric at all frequencies of current interest. It thus becomes an important possible candidate for a wide range of practical devices such as memories and signal processing devices in inexpensive form which could work in field or industrial environments. One question regarding the ultrasonic properties of PVF_2 has not heretofore been addressed. This is the question of the propagation loss of high frequency acoustic waves in such films. We have made the first reported measurements of the acoustic Q of this material, by measuring series and parallel acoustic resonances in poled samples of 25 μ thickness having evaporated conducting electrodes on the film faces. We have observed unloaded Q's of approximately 10 at a frequency of 40 MHz. This work will continue, using samples of different origin, processing and configuration, from which determinations will be made of its useful range of frequencies and applications.

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3. W. L. Bond, "The Measurement of Curvature and Prism Angles - Chapter XII," Microwave Laboratory Report No. 2343, Stanford University (September 1974).
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5. J. Fraser, J. Havlice, G. S. Kino, W. Leung, H. J. Shaw, K. Toda, T. Waugh, D. K. Winslow, and L. T. Zitelli, "A Two Dimensional Electronically Focused Imaging System," Microwave Laboratory Report No. 2378, Stanford University (November 1974).
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56. MECHANICAL BEHAVIOR OF SOLIDS

O. D. Sherby, Professor, Materials Science and Engineering

Research Associates:

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S. L. Robinson
B. Walser
R. Whalen

Graduate Students:

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L. L. Clements*
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I. C. Huseby*
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R. H. Klundt
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Y. Monma
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R. A. White

**Received Master's degree during report period.
*Received Ph.D. degree during report period.

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NASA-NGR-05-020-671
AT(04-3)-326 PA-38
Electric Power Research Institute

Research Report:

(1) Mechanical Behavior of Composite Materials
(with John C. Shyne, Professor, Materials Science and Engineering)

Graduate Students:

J. Lin
S. L. Robinson
R. Whalen (Research Associate)

Technical Objective:

The program centers on the mechanical behavior of particulate composite materials, with special emphasis on the influence of hard particles on the strength and ductility of close packed base metals.

Approach:

Techniques are being developed for the preparation of composite materials by powder metallurgy methods. Use is being made of a mechanical attritor for refining and mixing of powders prior to sintering and of a hydrostatic extrusion press for mechanical working difficult to shape particulate composites. The mechanical behavior of solids are being assessed by means of constant strain rate and constant stress creep tests. The elastic behavior of the composite materials also will be studied.

Progress:

The high temperature strength of metallic alloys can be improved by the addition of fine particles of a second hard phase. Research is underway on the mechanism of strengthening of zinc, cadmium and magnesium composite materials. Composites of Zn-W, Zn-Al_2O_3, Mg-Fe, Mg-B and Cd-B (with up to thirty per cent of the second hard phase) have been prepared by a unique powder metallurgy-mechanical comminution processing treatment developed at Stanford University. In addition, we are investigating composites based on brass (70 Cu: 30 Zn) containing alumina particles.

The deformation behavior of zinc containing fine particles of alumina (0.3 microns) in large amounts (30 volume per cent) is highly anomalous. At temperatures in the vicinity of 0.4 T_m (T_m = absolute melting temperature) and the strength of zinc is decreased by the presence of the alumina particles, but the tensile ductility is improved. At temperatures at and above 0.5 T_m, however, the zinc-alumina composites are considerably stronger than pure zinc. Such large volume fraction particulate composites appear to exhibit a "threshold creep stress". That is, it appears that such materials may not creep below a certain critical stress; this is indeed a very desirable characteristic from the view point of alloy design for elevated temperature applications. A model is being developed to explain these results on the basis that particles are the only sources of dislocations. The model is similar to the Ansell-Weertman theory for dispersion hardened materials and explains quantitatively the results obtained.

Elastic property characteristics of the composite material are being assessed. Exceptionally high elastic stiffness materials have been prepared by the addition of boron particles to magnesium. A magnesium -25 v/o boron alloy has been developed with a modulus of 11.4×10^6 psi. This value is about double that for most commercial magnesium alloys although the ductility is low (5% compression deformation is only possible before cracking occurs). Research is now being extended to Mg-Li solid solution alloys containing boron particles. Current results on a Mg-Li (15 at % Li) solid solution alloy containing 25 v/o boron have revealed very promising mechanical characterisitics; the elastic stiffness is over 12 x 10^6 psi, and the ductility of the composite in compression tests is very high (no fracturing after 50% deformation). The type of materials we have developed would suggest a new class of technologically useful materials, namely, particulate composites containing large volume fractions of hard second phase.

(2) Hydrostatic Extrusion
(with John C. Shyne, Professor of Materials Science and Engineering and Erastus H. Lee, Professor of Applied Mechanics)

Graduate Students:

R. Caligiuri
L. Eiselstein
R. Mallett (Research Associate)
R. Whalen (Research Associate)

Technical Objective:

To determine the advantages and disadvantages of hydrostatic extrusion as a means of improving the properties of extruded materials. The frontier of hydrostatic extrusion in forming materials not extrudable by normal extrusion processes will be investigated. Comparison of hydrostatic extrusion with other large strain forming operations, such as wire drawing and rolling, will be made.

Approach:

This research has as its aim the study, both analytical and experimental, of the mechanics of the hydrostatic extrusion process, and the application of hydrostatic extrusion to the preparation of wrought materials of superior properties.

Progress:

We will be investigating the response of a variety of materials to hydrostatic extrusion. The microstructure and mechanical properties of extruded materials will be related to the important processing variables, extrusion ratio, extrusion pressure, temperature, and extrusion rate. The experiments fall into two categories: 1. A detailed, systematic investigation of the influence of the processing variables on the properties of several fairly simple materials (pure Fe, Ni, Mg, and Ti; and Cu-30Zn or Cu-10Sn) 2. The utilization of hydrostatic extrusion to optimize the properties of more complex materials chosen for their technological utility (Mg-Li-B for high specific stiffness; Fe-C for high strength, ductility; T-D Nichrome for high temperature strength; Al-Fe alloy for high strength, high conductivity material; NbTi a super conducting alloy).

(3) Deformation of Materials at High Strain Rate at Warm and High Temperatures

Graduate Students:

S. Kayali
R. Klundt
B. Walser (Research Associate)
R. White

Technical Objective:

To study the mechanism of deformation at high strain rate at warm and high temperature. Study of the mechanical behavior of unusual structures developed by thermal-mechanical processing operations with special emphasis in the warm working range of temperatures where subgrains and/or fine grains are developed.

Approach:

Constant strain rate tests and special thermal-mechanical processing treatments are used with the objective of developing ultra-fine-structures. A rapid quenching technique during high strain rate torsional deformation has been devised to assess the deformation mechanisms of warm and hot working. Superplastic characteristics of fine grained materials are being studied by means of tension and compression testing.

a. Development of controlled fine structures by thermal-mechanical processing.

We have been attempting to develop particulate composites in ultrahigh carbon steels by special thermal-mechanical treatment (TMT) processing. Our research has centered on plain carbon steels containing 1.3 to 2.3% carbon (twenty to thirty-five volume percent cementite respectively). Much of our basic studies in the past years related to strain-enhanced spheroidization, warm working, strain created vacancies and superplasticity proved indispensable in our attempt to obtain fine grained structures in ultra high carbon steels. Various TMT processing procedures have been developed which have resulted in particulate composites of cementite in iron containing ferrite grains finer than one micron in size. Such high carbon steels are superplastic at warm temperatures (over 750% elongation has been achieved). Furthermore, they can be made strong and ductile at room temperature; for example, a 1.3% carbon steel, processed to consist of fine spheroidized cementite with accompanying fine ferrite grains, exhibits a yield strength of 150 ksi, an ultimate tensile strength of 200 ksi and 15 percent elongation. To the best of our knowledge this is the first time plain carbon steels have been made superplastic and our results suggest exciting possibilities in the application of inexpensive steels for many new structural applications.

We are investigating the influence of background impurity content (principally Mn and Si) on the superplastic characteristics of the ultrahigh carbon steels. Current results indicate that it is not possible to make such Fe-C alloys superplastic when they are pure; this unexpected result is attributed to the ease of grain growth in such materials. Dilute alloying with chromium is being considered as a means of enhancing the properties of the ultrahigh carbon steels through suitable heat treatment after superplastic forming.

The ease of deformation of superplastic materials would suggest that such materials, when in powder form, can be sintered readily under low pressures. We are investigating the sintering characteristics of such materials. Preliminary results on powders of a 2.6%C cast iron suggest that "superplastic sintering" may indeed be feasible; future studies will include ultrahigh carbon steels which we have already shown to be superplastic.

Using a Pb-Sn eutectic alloy as a model system, we are attempting to determine why concurrent straining enhances the rate of spheroidization. We are also studying the superplastic characteristics of this alloy when in a fine spheroidized state and are attempting to develop an atomistic model to explain superplastic flow of metallic base alloys.

b. Mechanism of warm and hot working in crystalline solids.

The factors influencing ductility and ductile fracture of materials at elevated temperature have not been studied extensively. Such studies are of paramount importance in assessing the formability of materials. A torsion apparatus has been developed at Stanford capable of deforming materials up to strain rates of 10,000 per cent per second and temperatures of up to 2200°F. One of the unique features of our apparatus is that samples can be quenched instantaneously after deformation. In this manner the exact mechanism of plastic flow during high strain rate deformation can be evaluated. We are also capable of simulating complex thermal-mechanical processing operations with small scale samples.

Our work has revealed that structural change during warm working of polycrystalline solids is characterized by the formation of well defined subgrains. The subgrain size developed depends primarily on the modulus compensated stress, $\frac{\sigma}{E}$, and is insensitive to solid solution alloying, crystal structure and stacking fault energy. Our results reveal that at low deformation stresses the subgrain size, λ, equals $4b\,(\frac{\sigma}{E})^{-1}$ where b is burgers vector and at high deformation stresses $\lambda = 10^{-2} b\,(\frac{\sigma}{E})^{-2}$. The nature of the subgrain boundary, however, appears to be a function of the temperature at which it is formed. For a given subgrain size, the higher the temperature of working the more effective is the subgrain boundary as a barrier to low temperature plastic flow. The ambient temperature strength of subgrain strengthened materials correlates well with the size of the retained subgrains, λ, and is shown to follow the relation $\sigma = \sigma_o + k\lambda^{-1}$ where σ_o and k are material constants. We have shown that subgrains are a more potent method of hardening than grains in the fine size range (ten microns and less). Studies include austenitic and ferritic stainless steels as well as several iron base binary solid solution alloys. Our work reveals that subgrains inhibit the yield point phenomenon in mild steels; this is an important observation and suggests a new method of developing non-aging steels.

We are studying the influence of large plastic strain (ε = 5 to 20) at warm temperature on the development, and nature of subgrain boundaries. Preliminary results on a ferritic stainless steel suggest that creep properties, as well as room temperature properties are influenced by the amount of warm working strain. This processing variable (of large strain deformation) at warm and hot temperatures has generally not been considered in technological applications and has not been studied academically.

(4) Mechanical behavior of polycrystalline solids at elevated temperatures.

Graduate Students:

J. Lin
A. K. Miller (Research Associate)
Y. Monma
S. L. Robinson (Research Associate)

Technical Objective:

To understand the mechanical behavior of polycrystalline solids at elevated temperature (0.4 to 0.9 T_m) under conditions of low stress (creep).

Approach:

Constant stress creep tests and constant strain rate tests are used to assess properties of both metallic and non-metallic polycrystalline solids.

Progress:

We have embarked on a study of the influence of texture on creep of anisotropic hexagonal close packed materials. We have found that extruded powder metallurgy zinc (textured with basal planes oriented radially to the extrusion axis) creeps fifty times slower in longitudinal samples than in transverse samples. This effect persists at temperatures from 0.4 to 0.9 T_m. We are currently attempting to understand the origin of texture hardening on creep and are considering the possible influence of subgrains, elastic anisotropy and slip anisotropy.

The creep behavior of metals that exhibit anomalous diffusion characteristics (exceptionally high diffusivities in relation to their melting temperatures) are being assessed. It is shown that the creep activation energy of these metals is equal to the corresponding self-diffusion activation energy. An unusual feature of these metals is that power law breakdown does not seem to occur at $\dot{\epsilon}/D = 10^9$ cm^{-2} as observed for most normal metals; this observation suggests that excess vacancy generation may not occur until very high stresses are applied.

The importance of subgrains on the creep resistance of materials is not well understood. Studies on pure aluminum and sodium chloride have been performed to determine the influence of subgrain boundaries on creep. Research to date suggest that the creep rate is proportional to the third power of the subgrain diameter at a given stress; furthermore, at a constant subgrain size, the stress dependence of the creep rate (in the power law range) yields a stress exponent of about seven or eight. There are no contemporary creep theories that can explain these results. The practical implications of our work is clear: if one can decrease the subgrain size by a factor of a hundred, the creep rate will decrease by a factor of a million. To retain fine subgrains for high creep resistance at a given stress it will be necessary to pin such boundaries. It is intended to investigate the influence of subgrains on the creep resistance of austenitic and ferritic steels.

We are attempting to determine the mechanism of creep flow in T-D Nichrome and other dispersion hardened materials. In this study, we are attempting to establish if a threshold stress for creep exists in T-D Nichrome since there is evidence for such behavior in high volume fraction dispersion hardened systems. Novel methods such as stress relaxation are being used to determine the stress exponent for creep as well as to determine the creep behavior at very low strain rates. Special emphasis will be placed on the possible importance of subgrain size on the creep resistance of T-D Nichrome; transmission electron microscopy will be used as a means of detecting such subgrain structures.

A phenomenological model to simulate the transient and steady-state deformation behavior of metals under complex load and temperature histories has been developed. Designated as MATMOD (for MATerials MODel), its major characteristics are (1) a unification of short-time plasticity, longer-time creep, and cyclic deformation into a single set of constitutive equations, and (2) the use of metallurgical structure as a primary variable. The model has been tested on aluminum, stainless steels, and a nickel-base superalloy and is being developed further for use with Zircaloy and eventual implementation into nuclear reactor performance and safety analysis codes.

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2. "The Influence of Strain-rate and Temperature on Mechanical Behavior in Polycrystalline Aluminum and Its Composites" (Hsu Shu-en, C. Y. Chen, . C. Yang and O. D. Sherby) Materials Science, 6, 1974, 167-174.

3. "Some Factors Influencing the Strain Rate-Temperature Dependence of the Flow Stress in Polycrystalline Solids" (O. D. Sherby and C. M. Young) ASM, John Dorn Memorial Symposium, 1975, 497-541.
4. "Elimination of Yield Point Phenomenon in Mild Steel by Warm Working" (C. M. Young, B. Walser, E. P. Abrahamson II and O. D. Sherby) Scripta Metallurgica, 9, 1975, 35-38.
5. "Superplastic Ultra-High Carbon Steels" (O. D. Sherby, B. Walser, C. M. Young and E. M. Cady) Scripta Metallurgica, 9, 1975, 569-574.
6. "Method of Making a Composite Alloy" (O. D. Sherby, I. C. Huseby and R. Whalen) U.S. Patent #3,827,921,August 6, 1974.
7. "Effect of Subgrain Size on the High Temperature Strength of Polycrystalline Aluminum as Determined by Constant Strain Rate Tests" (C. M. Young , S. L. Robinson and O. D. Sherby) Acta Metallurgica, 23, 1975, 633.
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10. "An Inelastic Constitutive Model for Monotonic, Cyclic and Creep Deformation: Part 2 - Application to Type 304 Stainless Steel" (A. Miller), ASME Reprint No. 75-Mat-15, presented at Conference on Micromechanical Modelling of Flow and Fracture, Troy, N.Y. June 23-25, 1975.
11. "On the Possible Role of Subgrain Broundary Strengthening in Creep of Dispersion Hardened Alloys" (S. L. Robinson and O. D. Sherby) talk presented at the annual AIME Meeting, Conference and Materials Science Symposium, October 21-24, 1974, Detroit, Michigan.

57. KINETICS OF SOME SOLID STATE REACTIONS

J. C. Shyne, Professor, Materials Science and Engineering

Graduate Students:

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*Received PhD during report period.

Agency Support:

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ONR N0001467 A 0112 0083
ONR N0001475 C 0662 with O. D. Sherby
ARPA through CMR
NSF through CMR

Research Report:

(1) The Influence of High Intensity Acoustic Radiation on the Kinetics of Solid State Processes

Graduate Student: F. C. Fehrer, Ph.D. graduate, January 1975

Technical Objective:

To observe and explain the influence of ultrasonic mechanical vibrations on the rates of some solid state reactions.

Approach:

High amplitude standing waves are developed in specimen materials using a 20 kc transducer. Isothermal reaction rates are measured as a function of reaction temperature and acoustical intensity.

Progress:

Experiments on 6061 Aluminum indicate that acoustic oscillation has a negligible influence on the kinetics of recovery of cold worked aluminum. Experiments to assess the acoustic hardening effect on pure copper are completed. It has been observed that for any given acoustic stress the acoustic hardening is greater the higher the temperature, (from -196°C up to 250°C, the maximum temperature at which specimens were oscillated). It was observed that acoustically oscillated Cu is hardened considerably more than the identical material strained in tension to the same stress. It appears that acoustically hardened Cu has a defect structure (many dislocation loop and dipoles) different from monotonically strained Cu but similar to that seen in fatigued specimens.

(2) Internal Friction of Materials

Graduate Student: R. J. Austin

Technical Objective:

To utilize mechanical damping measurements to study diffusional processes, internal interfaces, and dislocation behavior.

Approach:

This is essentially absorption spectroscopy in the acoustical frequency range. The decay in amplitude of specimens vibrating in free decay is measured as a function of frequency and temperature.

An inverted torsion pendulum has been constructed and completely calibrated. This has been used for the study of thermally activated dislocation movement. Wire specimens of high purity Au and Al have been prepared with a bamboo grain structure for this purpose.

The results to date on high purity Al indicate that the background damping of Al in the range from about 80°C to 350°C is caused by thermally activated dislocation movement. Some peculiarities have been observed relative to the effect of recovery on this mechanical damping; this has been further explored by making comparable measurements on Al with controlled amounts of impurities and by comparison with the reported recovery differences of high purity and impure Al.

Progress has been made toward investigating models for the observed experimental damping by computer simulation.

(4) Mechanical Behavior of Composite Materials

(with Professor O. D. Sherby)

Graduate Student: I. C. Huseby, Ph.D. degree granted January 1975

The influence of a second phase on the strength and ductility of hexagonal metals is being studied. Composits of magnesium, zinc, beryllium or cadmium containing tungsten Al_2O_2 or other dispersed second phase are prepared by powder metallurgy techniques. Mechanical testing in tension and compression over a range of test temperature is performed. Results indicate that mechanical twinning determines the plastic behavior in the case of Mg base alloys.

In contrast to Zn base particulate composites, Mg base composites containing Fe, W, MgO or B show decreased ductility compared to pure Mg. It has been found that many of the mechanical characteristics of the Mg base composites depend critically upon the deformation texture that develops in the material.

(5) Decomposition of Lamellar Microstructures

Graduate Student: M. Shimizu

Lamellar polyphase microstructures are common in alloys; the most familiar example is pearlite, the eutectoid of Fe_3C and α-Fe found in steels. This research is intended to investigate the mechanism and kinetics of the decomposition of such microstructures after plastic deformation. The subject material is the Pb-Sn eutectic. Attempts to use differential thermal analysis to follow the decomposition reactions during heating after cold working the Pb-Sn eutectic at -77°C have been unsuccessful. The small exothermic heat of reaction is confused by experimental noise. Also there is evidence that the breakdown of the cold worked lamellar eutectic microstructure proceeds at -77°C. Therefore current efforts are being directed at the measurment of deformation properties of the Pb-Sn eutectic at low temperatures and the correlation of this mechanical behavior with the subsequently observed microstructure at room temperature.

59. ULTRA-SHORT OPTICAL PULSE GENERATION AND APPLICATIONS

A. E. Siegman, Professor of Electrical Engineering

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Agency Support:

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Technial Objectives:

To generate the shortest possible picosecond light pulses on a continuous wave and tunable basis; and to use these pulses in making significant physical measurements on materials, particularly materials of biochemical and biophysical interest.

Approach:

The development and use of a transient-grating picosecond light scattering technique, together with a repetitively Q-switched mode-locked laser, is being applied to the measurement of ultrafast physical and photochemical processes.

Research Report:

Our group has made significant contributions over the past several years to the development of the laser mode locking techniques that make possible the generation of continuous trains of extremely short optical pulses (pulsewidths less than 30 psec). By using these extremely short optical pulses, both to excite atomic and molecular systems, and then to probe the changes in the optical properties (e.g., change in the complex susceptibility tensor) of the excited systems, one can potentially make time resolved measurements of atomic and molecular properties (such as relaxation times and reorientation times) with picosecond time resolution. This degree of time resolution is inaccessible using conventional optical detectors and optical pulse measurement methods.

Picosecond pulses with high peak powers, have been achieved in the visible (5320 Å) and the UV (3547 Å, 2660 Å), as well as in the IR (1.064μ). From this work, a theoretical understanding of the transient buildup of mode-locked pulses has been attained.[1] A $LiNbO_3$ electro-optic switch driven by an avalanche transistor switch has been constructed to gate out a single pulse in each train of mode-locked pulses comprising each Q-switched pulse.

Two pulses from the same laser arriving at an experimental sample coincident in time but from slightly different directions can produce excited states or other photo-excited effects in the form of an induced grating or a transient hologram pattern in the sample. A variable-delay laser probe pulse can then be diffracted by the photo-induced grating.[2,3,4] By using a repetitive train of short pulses and measuring the diffracted probe beam intensity averaged over many pulses, while slowly varying the time delay between excitation and probe pulses, one can measure the decay of the photoexcited phenomenon in stroboscopic fashion, with a time resolution approximating the laser pulsewidth. We have now carried out preliminary measurements of molecular relaxation times using repetitive mode-locked laser pulses[5] plus such a transient-grating apparatus designed to measure a wide variety of subnanosecond to picosecond phenomena.

Our apparatus uses a continuously pumped, repetitively Q-switched, actively mode-locked Nd:YAG laser[5,6] which produces bursts of 20 to 30 mode-locked pulses with several hundred kilowatts peak power and durations of ~ 50 psec at repetition rates up to 500 Hz.

The pulses from this laser enter an optical system which produces two excitation beams and a variable-delay probe beam intersecting at a common point. Our transient-grating measurements to date were made with two excitation beams separated by 53 mrad, together with a central probe beam, all focused to a ~ 70 μm gaussian spot size in a 125 μm thick dye cell containing a 10^{-4} M solution of Rhodamine 6G in methanol, ethanol or 1-propanol. The dye cell was rotated slowly to avoid photodecomposition of the dye. A transient grating with a 10 μm spatial periodicity was produced in the dye cell by excitation ay 532 nm from the ground singlet S_0 to the first excited singlet state S_1 . This grating could be photographed through a microscope by its own fluorescent emission.

Diffraction of the probe beam from this grating resulted from the difference in absorption cross section of the S_0 and S_1 states for the 532 nm probe wavelength.[7] In fact, the two excitation beams by themselves first produced two strong self-diffracted beams located an additional 53 mrad outside each of the two incident beams. For any delay greater than zero the probe beam then produced two readily visible diffracted beams corresponding to the +1 and -1 orders of the induced grating produced by the excitation beams, as well as self-diffracted cross-product beams between the probe and each excitation beam.

The normalized intensity of one of the diffracted probe beams versus the probe pulse delay, time-averaged over many pulses, is proportional to the amplitude of the decaying transient grating squared times the incident pulse intensity P_0 . For the dye solution studied in these experiments the grating amplitude depends on the decay of the population difference (and on the absorption cross-section difference) between S_0 and S_1 singlet levels, suitably averaged over the orientational distribution of the molecules.[4,8,9,10] The decaying portion of the scattered signal contains two times constants τ_s and τ_{rot} , where τ_s is the upper singlet fluorescence lifetime and $\tau_{rot} \equiv (6D_{rot})^{-1}$ is the orientational relaxation time.

Table I summarizes our results for Rhodamine 6G in three different solvents. Within experimental accuracy the rotational relaxation times agree with those measured by Chuang and Eisenthal.[9] Except for the methanol solution, which displays an unexpectedly short lifetime, the values for the fluorescent lifetimes are also reasonable.[11-14] Alfano, Shapiro and Yu[11] have measured the lifetime of Rhodamine 6G in ethanol and find it increases from 3.1 nsec for concentrations below 10^{-5} M to a maximum of 4.8 nsec at 2×10^{-4} M and then decreases rapidly at higher concentrations. Rehm and Eisenthal[12] measured a lifetime of 4.2 nsec for Rhodamine 6G in glycerol at low concentrations. Mack[13] and Theiss and Weber[14] measure values of 5.5 and 5.8 nsec in low concentration ethanol and methanol solutions.

We believe the transient grating technique used here can be useful as a method of excited-state spectroscopy for a wide variety of similar experiments involving molecular states, excited states in semiconductors, excitons in molecular crystals, nonradiative relaxation rates, and energy transfer studies. Because one detects a small scattered probe signal against a dark background, rather than looking for a small change in a large (and possibly noisy) probe beam, the transient-grating method can offer improved sensitivity and background rejection. Because a phase grating will diffract the probe beam as well as an amplitude grating, one can probe excited-state dispersion as well as absorption effects. By varying the beam angles and thus the grating spacing, one can separate spatial diffusion from lifetime effects in the grating relaxation; and by rotating the fringe direction relative to the sample, one can study anisotropic diffusion effects.

At this stage of the research, we are preparing the experimental setup for exciton migration studies in molecular crystal at low temperatures, as well as several other excited state spectroscopy measurements in the picosecond range.

TABLE I

Experimental Results for the Singlet State Lifetime τ_s and Rotational Relaxation Time τ_{rot} for Rhodamine 6G in Several Alcohols

Solvent	R6G Concentration	τ_{rot}	τ_s
Methanol	$2.0 \cdot 10^{-4}$ M	140 ± 30 psec	1.7 - 2.0 nsec
Ethanol	$1.0 \cdot 10^{-4}$ M	300 ± 50 psec	3.7 ± 0.5 nsec
1-Propanol	$1.0 \cdot 10^{-4}$ M	500 ± 100 psec	3.8 ± 0.5 nsec

Also, other experiments are being prepared, namely measurements of Kerr coefficients. A process of further shortening the 30-50 psec pulses is being also planned, by using a Gires-Tournois interferometer inside the laser cavity for pulse narrowing.

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59. ELECTRON SPECTROSCOPY, SURFACES, AND INTERFACES

W. E. Spicer, Professor of Electrical Engineering and Materials Science

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Technical Objective and Approach:

To apply the newly developed tools of electron spectroscopy (Photoemission, Auger, etc.) together with other techniques such as temperature programmed desorption to the study of surfaces and interfaces. Particular attention is given to fundamental problems which can have strong practical impact, e.g., in catalysis and semiconductor devices.

Research Report:

(1) Studies of Pt with Regard to its Special Catalytic Properties

D. M. Collins, J. B. Lee

There is considerable interest in the surface electronic structure of platinum due to its extraordinary properties as a catalyst. It is known to catalyze a wide variety of reactions, including some, such as the hydrogenation of oxygen to form water, for which it is one of the very few known catalysts. These unusual properties make platinum a prime target for research related to catalysis, particularly in veiw of the recent energy shortage.

We have combined ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), and temperature programmed desorption (TPD) to study the properties of simple gases (CO and O_2) adsorbed on a polycrystalline platinum ribbon and to monitor the reaction of hydrogen with oxygen adsorbed on platinum. The use of all these techniques was necessary to fully characterize the sample.

AES was used to determine the cleanliness of the platinum and to guide the development of a cleaning procedure which yielded atomically clean platinum surfaces. The cleaning procedure developed consisted primarily of heating the platinum ribbon in oxygen; a procedure which has been shown to result in a predominantly (111) orientation of the polycrystalline ribbon.

The use of UPS in conjunction with TPD allowed us to correlate the changes of the photoemission energy distribution curves (EDCs) with the coverage of carbon monoxide and oxygen. Our TPD results were in agreement with those of other workers which showed two dominant binding states for both carbon monoxide and oxygen adsorbed at 29[illegible]° K. The two states have been designated the β state (the more tightly bound state, ~ 32 kcal mole^{-1} for CO and ~ [illegible]2 kcal mole^{-1} for O) and the α state (the less tightly bound state, ~ 2[illegible] kcal mole^{-1} for CO and ~ 4[illegible] kcal mole^{-1} for O). The β state is the first to fill, with the α state filling only after the β state nears saturation coverage.

For both carbon monoxide and oxygen, the changes in the UPS EDCs saturate after the filling of the β states. That is, the filling of the α binding states results in no further changes in the EDCs. This is very interesting in light of the fact that the binding energies of the α states for both carbon monoxide and oxygen are only 10% to 20% smaller than for the respective β states and are thus still quite tightly bound.

It is also interesting to note the qualitative differences observed between carbon monoxide and oxygen in the UPS data. The adosrption of carbon monoxide results in a predominant drop in platinum valence band emission near the Fermi level and the appearance of a peak associated with carbon monoxide molecular orbitals or platinum-carbon monoxide bonding orbitals approximately 8 eV below the Fermi level. In contrast with this, for oxygen adsorption, there is a relatively uniform decrease in emission from the platinum valence band and no structure associated with oxygen electronic states is observed.

The results for carbon monoxide on platinum are typical of what is seen for most simple gases on d-band metals. The oxygen results, however, are quite different. We believe the unusual results for oxygen represent a first order effect which reflects the unique properties of the platinum-oxygen bond which give rise to platinum's remarkable properties in catalyzing reactions involving oxygen, such as the oxidation of carbon monoxide to form carbon dioxide and the hydrogenation of oxygen to form water.

By using the changes in the EDC of oxygen adsorbed on platinum, resulting from hydrogen exposure, as a measure of oxygen coverage, we were able to follow the reaction of hydrogen with adsorbed oxygen and thus arrive at a probable mechanism for the reaction. For oxygen atoms occupying only the β state, which corresponds to $\sim 2 \times 10^{14}$ atoms cm^{-2} as determined by TPD, we were able to show that ~ 0.7 oxygen atoms were removed for each hydrogen molecule incident on the surface. This reaction probability is much higher than has been found by less direct methods.

We believe that the mechanism of the water reaction on platinum is analogous to a group of chemisorptions known as the fast non-activated chemisorptions. The mechanism for this process consists of a physically adsorbed precursor state in which the atom or molecule is mobile enough that it may encounter a binding site and thus chemisorb. In the case of the hydrogenation of adsorbed oxygen, the binding site is replaced by an adsorbed oxygen atom and the chemisorption step is replaced by the formation of water. In order for the reaction probability to be as high as that found here (0.7 oxygen atoms removed for each hydrogen molecule incident on the surface), it is evident that the "short term" sticking probability for hydrogen physisorption must be high and that the mobility and residence time of the physically adsorbed hydrogen molecule must permit enough encounters with adsorbed oxygen atoms to allow a high probability for the formation of water. It is clear from the EDCs and TPD measurements made following the reaction that the water desorbs following its formation.

Future plans include similar studies of single crystal platinum surfaces, in particular the (111), (100), and 6 (111) × (100) stepped surfaces. We also intend to study the H_2O reaction on tungsten carbide by the methods developed, since (see the next section) WC has been shown to exhibit platinum-like behavior in catalyzing the water reaction.

(2) Studies of Tungsten Carbide as a Substitute for Pt Catalyst

I. Lindau, J.B.Lee, D.M.Collins, K.Y.Yu,
D.Ling, J.Miller, C.M.Garner

Professor Michel Boudart and his group have evidence that tungsten carbide catalyzes the hydrogen oxygen reaction the same way as Pt. The work here is part of a larger project. The overall supervision of M.Boudart to further explore this and to attempt to develop practical tungsten carbide catalyst. The study of the hydrogen oxygen reaction discussed in the preceding section was partially supported by this work. The motivation being to understand the reaction on Pt and the relationship between the Pt electronic structure and the reaction in order to understand studies undertaken on tungsten carbide.

In addition to the Pt work, we have studied the electronic structure of tungsten and the reaction of the surface tungsten with both carbon and oxygen. Both the conventional equipment in the on-campus laboratory and the new synchrotron radiation facility were used in these studies. One object of the work was to see if the core shifts of the tungsten could be observed in the 30-300 eV range due to the addition of carbon or oxygen to the surface. Clear shifts were detected on the addition of oxygen but not on the addition of carbon. Present indications are that this was due to the fact that the oxygen makes a strong chemical bond at the surface whereas the carbon studied was of a graphitic nature which did not bond strongly with the surface. We believe these results are very significant and that they show that the synchrotron radiation facility can be used to study chemical shifts as well as change in the valence band. The importance of the flexibility given by the continuous wavelength tunability of this source cannot be over emphasized.

Bulk samples of tungsten carbide are being prepared in another phase of this work and will be studied shortly.

(3) Studies of Surface Adsorption and Reaction with Relation to Catalytic Processes

I.Lindau, K.Y.Yu, P.Pianetta, D.Ling, J.
Miller, C.M.Garner, S.F.Lin, D.Collins, P.
Chye

The objective of the work reported here is to better understand the adsorption of gases on metals and alloys; to better understand catalytic reactions on such substrates, and to relate this work to important practical catalytic systems. Models systems have been studied at the beginning of this work in order to "calibrate" ultraviolet photoemission spectroscopy (UPS) which will be a major tool in this investigation. The first system studied was an ideal physical adsorption system in which seven different gases were adsorbed at low temperatures on the cleavage face of MoS_2. This substrate was chosen because, to the first approximation, there are no unsatisfied chemical bonds in the cleavage face, i.e., the material is mica like with all the bonding in the two dimensional plane and these planes held together by Van der Waal forces. These studies established that the UPS spectra of physisorbed gases is a broadend spectrum of the free gas spectra with the difference that the ionization energy is reduced by approximately 1.5 eV. The individual reductions for each of the seven gases have been tabulated as well as the change in work functions for the photoemission substrate. Of particular interest is the question as to whether emission from the substrate is strongly affected by either interferences between substrate and adsorbed gas emission or by attenuation of the electrons in passing through the adsorbed gas. Even in cases where so much gas was adsorbed the spectrum of the adsorbed gas was several times that of the substrate, the substrate emission was found to be essentially unchanged. We have studied the adsorption of a number of gases on metal substrates. In almost all cases very striking changes were observed in the emission from the substrate. This emission was found to be essentially independent of photon energy over a range more than 10 eV and to depend strongly in most cases on the adsorbed gas. All of these results argue strongly that the changes in the substrate emission are not due principally to interference or scattering effects but are a reflection of the change in the electronic structure of the substrate brought about by the hybridization between the chemically adsorbed molecule and the substrate.

Other workers have suggested that in certain cases the chemical adsorption energy can be quantitatively measured by the shift in energy of the orbitals involved in the bonding. Implicit in their suggestion is the conclusion that the changes in the substrate does not have to be taken into account in determining the energy. Their work was based on the adsorption of several gases on nickel. To test this conclusion we studied CO, C_2H_2 and C_2H_4 adsorbed on iron and copper. These materials were chosen because the typical adsorption energies on copper are roughly one third that on nickel or iron. Our results show that the conclusions of the previous group were incorrect. We conclude from all of these studies that the chemical bonding can only be understood by understanding the change in the electronic structure at the substrate due to the hybridization. Further, we conclude that UPS CAN give important experimental data in this regard. We are working to develop strong contacts with a number of theoretical groups including that of Walter Harrison at Stanford in order to gain further insight in these processes.

A third approach taking in this work is the study of CuNi alloys since it is believed that in the future alloys or composite materials have a large future in the development of new catalytic materials and also because we believe that the alloys give promise in studying the local nature of chemical adsorption. We have established that in the Cu-Ni system the surface is copper rich and have obtained quantitative data through Auger spectroscopy on the surface vs bulk composition. Through thermal desorption studies we have established that a surface which contains approximately 30% Ni does not exhibit any appreciable region with the chemical adsorption characteristic of Ni and that it is also quite different from pure copper. Thus we conclude that the surface is basically a random alloy and that the chemical bonding at specific sights is determined by the local composition at those sights. In order to pursue these studies further, it has been necessary to construct new equipment which is nearing completion and the studies will go forward as soon as possible.

(4) Synchrotron Radiation Studies of Metals

I. Lindau, P.Pianetta, K.Y.Yu

In order to test the abilities of the new facility at SLAC, the Stanford Synchrotron Radiation Project (SSRP), which provides continuously tunable radiation in ultra high vacuum between 6-300 eV (this range will ultimately be extended to approximately 1000 eV), studies have been made with gold and a number of other materials in the range from 30 to 300 eV and in the range from 6-20 eV. The results are generally encouraging and the number of interesting new phenomena have been uncovered is mentioned in other sections of this report. We are beginning to use this facility extensively in our research and this use should be extended a great deal in the coming months.

(5) Surface and Interface Studies of III-V Compounds

W.E.Spicer, P.Gregory, P.Chye, I.A.Babalola
T. Sukegawa

Based on the work done under this contract during the previous fiscal year, a model was proposed for the (110) surface of GaAs. In this model, the empty surface states were associated with the Ga surface atoms and the filled surface states with the As surface atoms and a band gap of considerable size (1 eV or larger) was found to occur between the filled and empty states. This model was due to Gregory, Spicer, Ciraci and Harrison. Based on data from Stanford, and a wide range of other laboratories, it is now impossible to extend this model to all faces of all III-V compounds. In the general model, the empty surface states are associated with the column III atom and the filled surface states with the column V surface atom and a large band gap is found to occur between the filled and empty states. For example, on the (111) face of GaAs, the empty surface states are found on the Ga side of the crystal, the filled surface state on the As side of the crystal. In general, it appears that the filled surface states lie below the top of the valence band and the empty surface states lie in the upper part of the hidden gap. However, cases may occur where the filled states extend into the band gap region and the empty states lie above the top of the conduction band.

Detailed studies have been made at Stanford on the (110) cleavage faces of InP and GaSb during this period. The filled surface states in both cases were found to lie below the top of the valence band. The InP empty surface states were found to lie 0.25 eV below the conduction band minimum. In GaSb, the empty surface states lie very close to or above the bottom of the conduction band.

The effect of Cs on the surface states, surface pinning of the Fermi level and the electronic structure at the surface have been studied in detail for GaAs and InP. Studies of GaSb are presently underway. For both GaAs and InP, the final Fermi state position after a monolayer of Cs applied is found to roughly coincide with the bottom of the empty surface states. However, quite strong interactions were found between the surface states and the Cs. For example, on p± material Fermi level is found to first rise to 0.7 eV above the valence band maximum with a fractional monolayer of Cs and then to decline and take up a stationary position approximately 0.1 eV below the bottom of the empty surface states after a monolayer of Cs is applied. Most strikingly the leading edge of the valence band emission is found to move up about 0.25 eV as the Cs coverage is increased up to a monolayer; that is, it takes approximately 0.25 eV less photon energy to remove an electron to a given final energy state at the interface than in the bulk of the material.

In order to correlate studies on Cs oxide covered photocathodes with knowledge of bulk Cs oxide we have studied the oxidation process of Cs. The oxide is found to move into the interior of the material leaving metallic cesium on the surface until the last step in the oxidation. A sharp minimum is found in the work function at approximately the point which the metallic Fermi level disappears. This minimum work function is 1 eV or less. Rich structure is observed in the photoemission from the oxide. This changes as more oxygen is added in accordance with the expectations since there are a number of different Cs oxides. Studies have also been made of thick Cs oxide on GaAs. Correlations are now being made between the two results. It appears that positive correlations will be possible but the analysis is still underway. The effect of sodium on GaAs has also been studied and it has been found to be quite different from that of Cs.

Oxygen, CO and atomic and molecular hydrogen have also been studied on GaAs. These studies are relevant not only to photocathode development but also to preparation of practical surfaces for bulk devices.

Preprints or reprints covering most of the material mentioned above in detail are available on request.

(c) Synchrotron Radiation Studies of the Surfaces of III-V Semiconductors

I.Lindau, P.Pianetta, K.Y.Yu, J.Miller

As mentioned above the synchrotron radiation source (SSRP) gives us a tremendous new ability. In this contract we will concentrate on the use of this capability to study the surfaces of the III-V materials. Preliminary studies on Ge show that one can follow the oxidation quite well by looking at core shifts in the material. We will attempt to obtain core chemical shifts to understand oxidation as well as formation of Schottky barriers with Cs and other metals. In addition, we will look at transitions to empty surface state, photoemission from surface states and a wide range of other effects. A chamber has been designed which can be used both in our laboratory and at SSRP. This will allow us to do photoemission measurements from the near ultraviolet to several hundred eV and also to do *in situ* on the same samples Auger, energy loss, and other studies. The chamber also gives us the capability of a wide range of surface preparation. The work under this contract will be correlated very closely with the GaAs studies under the ARPA support mentioned as section 1 in this report (Spicer). A chamber has been completed and preliminary measurements should get underway by July, 1975.

(7) Studies of the Surface of Crystalline and Amorphous Si, ZnO, SrO and Related Materials

I.Lindau, R.Powell, J.Johannessen, D.Weismann

Studies of amorphous Si and comparison with results from crystalline Si indicate very strongly that surface state on amorphous materials are very different from that on the crystalline materials. Filled states apparently do not lie in the band gap of the amorphous material as they do in the crystalline material. These are preliminary results. Further studies will be undertaken. Studies of $SrTiO_3$ show no evidence for the high density of surface states predicted in the literature. This is very important since these surface states may have important consequences for possible catalytic materials.

Studies have been made of SiO_x (x-2) to correlate with studies of Auger emission in practical devices. Results appear consistent with Auger results which indicate that the sub oxides are made up of a SiO_2 matrix in which small clumps of amorphous Si are imbedded. This work is continuing. Preliminary studies in cooperation with Varian Associates using Auger and sputtering ion spectroscopy have given insight into the interface between Si and SiO_2 which characterizes practical MoS devices. It is found that the interface face is probably rough with a transition region of about 30 Å. However, the actual transition between the semiconductor and the oxide at any one spot is probably of the order of 5 Å - 10 Å. Evidence has been found of amorphous Si inclusion of the order of 10 Å or larger occuring near the interface. These results are very preliminary and will be pursued strongly in the future under a new joint program with Varian sponsored by ARPA.

Work on the anomalous temperature dependence of the thallous and copper halides, started under other support, has been completed and publications will appear soon.

(8) Organic Quasi One-Dimensional Compounds

S.F. Lin

This work has been funded previously by CMR and has been completed. One publication appeared in March and another has been accepted by Physical Review. Additional details on these studies of TTF-TCNQ, TCNQ and Cs-TCNQ are available on request.

(9) Investigation of Tin Oxide and Related Oxides with Regard to Cold Cathodes

R. A. Powell, D. Weissman

Tin oxide films have shown promise as cold electron emitters, i.e., cold cathodes. This was first reported by Russian workers, however during the last year very encouraging work has been obtained by Beta Industries under DOD support in this country. The objective of this work is to try to better understand the mechanism of emission in these cold cathodes. We have carried out UPS measurements on pure Sn surfaces and have made extensive studies of the oxidation of Sn and have studied the practical films formed by Beta Industry for cold cathodes before activation and have annealed these samples up to 800° C to study the effect of this step in activation. We find that Sn films tenaciously resist oxidation but that thoroughly oxidized films can be formed by evaporating in an oxygen pressure followed by annealing in an oxygen atmosphere. Details of the changes in the electronic structure with oxidation have been obtained. X-ray studies were made of the tin oxide formed *in situ* in our laboratory and tin oxide supplied by Beta Industries and significant differences found. Detail photoemission studies have been made on all samples. Particular attention has been made on the comparison of the SnO_2 films prepared by Beta Industry and by ourselves. In both cases, photoemission is found to occur from throughout the forbidden gap indicating a high level of states in the gap and the Fermi level is found to be approximately at the conduction band minimum. However, the Fermi level is found to be approximately 0.1 eV higher in the *in situ* formed samples than in the Beta Industry samples. The overall EDCs from the Beta Industry samples were quite different from our _in situ_ oxidized samples until the Beta Industry samples were annealed at between 600-900° C, then the EDCs were found to be quite similar. The results suggest the possibility that annealing of the Beta Industry samples provides a Sn rich surface. This will be further pursued in the future by use of new equipment which is underway which will allow us to do Auger spectroscopy on the surfaces and study the changes with various processes. We have proposed one model for the cold emission from tin oxide. Other groups have proposed several other models. Our future experimental work as much as possible will be aimed at distinguishing between these models in order to develop a more definitive model for the cold emission. Without such a well established model it appears very difficult to properly engineer the cathodes and to predict their ultimate performance and usefulness.

60. SOLID STATE PHYSICAL CHEMISTRY

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Agency Support:

NSF through CMR
ERDA at (04-3) 326 PA-37
Stanford Research Development Fund - 2-DHZ-057
Office of Naval Research - N00014-67-A-0112-0082

(1) Diffusion of Oxygen in Liquid Metal Systems

Objective and Approach:

This program applies solid state electrochemical techniques to the diffusion of oxygen in liquid metals, particularly those liquid metal systems forming stable oxides. This work is relevant to a number of practical phenomena, for example, deoxygenation of liquid metals, and liquid metal corrosion.

This study employs solid oxide electrolytes, such as calcia stabilized zirconia (CSZ) and yttria doped thoria (YDT). These oxides have the characteristic of essentially pure ionic conductivity at elevated temperatures over a range of temperatures and oxygen chemical potentials. The basic electrochemical cell includes a liquid metal electrode, M(L), the solid electrolyte, such as YDT, and a reference oxide electrode, such as Pt, CO/CO_2. The experimental approach utilizes the potentiostatic technique and the appropriate analysis of the current-time relationship for the potentiostatic operation of the cell allows computation of the diffusion coefficient.

Research Report:

The reliability of the experimental apparatus and approach was first established by the measurement of diffusion coefficients of oxygen in previously studied systems. Subsequently, the diffusion of oxygen in the Ga-In liquid alloy system was studied. This system is of interest because of the unexpectedly large difference in the diffusion coefficient for the two pure liquid metals. Five compositions have been studied to date and it was shown that a large change occurs with the first five atomic percent Ga added to In. Further study of this system is in progress. Future work will also include fundamental studies of the solid electrolyte, with specific reference to its practical utilization in electrochemical cells.

(2) Analysis of Dynamic Reacting Systems using Mass Spectrometric Techniques; Control of Impurities in the Epitaxial Growth of High Quality GaAs

Purpose and Approach:

The purpose of this program is to develop techniques for analyzing dynamic high temperature reacting systems using a molecular beam mass spectrometry. The specific system in question is a GaAs liquid phase epitaxial growth system and the associated chemical transport reactions. These reactions involve the protective atmosphere, the reactor walls and the crucible materials and are important sources of contamination during the epitaxial growth process. The present program is directed toward a quantitative study of this phenomena by analyzing the thermodynamics and kinetics of possible transport reactions. The practical relevance of this program is the obvious need to control impurity levels in semiconductors which are used for devices.

Various gas-solid interactions are selected which are relevant to liquid phase epitaxial growth, for example: fused quartz-graphite-hydrogen; high purity alumina - boron nitride - argon. The vapor species in these systems will be analyzed with a specially designed sampling probe which forms a molecular beam of a representative sample and introduces it into a quadrapole mass analyzer. The ultimate objective is to identify sources of impurities, determine their influence on the electrical properties of GaAs, and learn how to control them by appropriate modification of the growth procedure.

Research Report:

The major initial activity has been devoted to the design and construction of the molecular beam-mass analyzer system. Related studies on the liquid phase epitaxial growth of GaAs has shown that dramatic changes in the GaAs layer properties can be produced by small changes in the pre-growth annealing conditions. For example, undoped GaAs can be changed from n-type p-type by altering the pre-growth annealing temperature.

(3) Chemical Vapor Deposition of Refractory Compounds of Variable Composition and Particle Size

Purpose and Approach:

The purpose of this program is to explore methods for producing compounds of variable composition and particle size using chemical vapor deposition (CVD) techniques. The influence of the following experimental parameters on the structure and chemistry of the deposits are being studied: the composition of the gaseous reactants; the total pressure; the temperature; and the temperature profile.

Research Report:

The recent activity on this program has resulted in the development of a versatile CVD reactor and the synthesis of a number of compounds, particularly BN, GaN and $Al_xGa_{1-x}N$, with particular emphasis on the synthesis of fine particles. Particles in the 50-1000Å range have been synthesized and isolated and it was found in many cases that the fine particles were amorphous. Two important areas of activity have evolved, namely, the development of techniques for trapping fine particles, and the development of techniques for characterizing the particle size and the structure of fine particles. In the former area, fluid trapping systems have proven to be the most effective. In the latter, transmission electron microscopy has been the most productive tool, however, x-ray techniques and infrared spectroscopy have also provided valuable additional information to characterize the particles.

(4) Vapor Growth and Structural Characterization of Heteroepitaxial Semiconductor Layers

Objective:

This program explores the interrelationship between the preparation of thin semiconducting films, their structure, and their electrical properties and device application. The program in progress is specifically directed towards the heteroepitaxial deposition of gallium nitride (GaN) films on sapphire substrates, with particular reference to the preparation of light emitting diodes.

Approach:

Gallium nitride layers are grown on sapphire substrates using the vapor phase reaction between gallium monochloride and ammonia, with careful monitoring of the significant growth variables. These films are characterized using a variety of techniques, which include: optical microscopy, scanning electron microscopy, and x-ray techniques. There is particular interest in the nature of the semiconducting-insulating (s-i) junctions formed in this material by doping GaN with Mg during growth. This junction structure is used to prepare violet light emitting diodes.

Research Report:

Current work has emphasized the development of more precise procedures for monitoring the growth conditions, specifically the improved measurement of growth temperatures, temperature gradients and flow conditions. An additional parameter that appears to be very significant is the catalytic activity of the growth environment for the decomposition of ammonia; decomposition, catalyzed by the container materials such as graphite, will influence the nitrogen activity and also the local temperature. A change in the morphology of the deposit, caused by this effect, was observed. The catalytic activity of the reactor environment is presently being quantified by titration of ammonia after transit through the reactor.

The morphology, epitaxial relations and the film perfection have been evaluated using scanning electron microscopy and Laue back reflection techniques. More recently, x-ray topographic techniques were developed as an additional evaluative tool.

61. FUNDAMENTAL ASPECTS OF REACTIVITY IN INORGANIC SYSTEMS

H. Taube, Professor of Chemistry

Professional Associates:

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Agency Support:

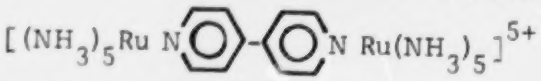
NIH GM 13638-10
NIH GM 22045-01
NSF MPS 7304859A01

Technical Objective:

Electron Transfer in Chemical Systems. Apart from the intrinsic interest in understanding what factors govern the direction and mechanism of electron flow between metal centers, the results are important in laying the foundation for understanding one of the major classes of chemical change, those involving oxidation-reduction. They are relevant also to understanding electronic conduction. In the simplest case, only two centers are dealt with, and the electron transfer process in such an instance can be regarded as an elementary step, subject to systematic study, a study which can help to relate electronic conductance to the fundamental properties of the component atomic centers. Furthermore, the way is open now to proceed by small increments to the study of multicenter systems and to make a systematic study of the transition from the two-center case to those in which electronic conduction as it is ordinarily understood is of interest.

Research Report:

In last year's report, mixed valence complexes of the class



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were referred to, in which the coupling between the metal centers, though strong enough to lead to an intervalence transition, is so weak the Ru(II) and Ru(III) character is virtually unaltered. The species

$$[(NH_3)_5Ru\ N{\equiv}C - C{\equiv}N\ Ru(NH_3)_5]^{5+} \qquad \text{II}$$

was also referred to. It is clear from recent measurements that in this species there is extensive valence delocalization. An important item of evidence in this context is that while N≡C- on Ru(II) shows a stretching frequency 350 cm^{-1} lower than N≡C- on Ru(III), in species (II) a single frequency is observed, lying between the values characteristic of Ru(II) and Ru(III). Thus we can conclude that electron transfer is more rapid than $350 \times 3 \times 10^{10}$ or 10^{13} sec^{-1}. This rapid "rate of electron transfer" explains why the nir band is independent of the dielectric properties of the solvent—solvent reorientation is on the time scale of only 10^{11} -10^{12} sec^{-1}. Chemical evidence points convincingly to the conclusion that there is strong valence delocalization in the mixed valence species. Ruthenium(III) promotes rapid hydration of the coordinated N≡C- while Ru(II) protects the group from attack by water. In the mixed valence species, the rate of N≡C- hydration is less than in a genuine Ru(III) complex by a factor of at least 10^4.

The highly delocalized system described provides the incentive for current work in which the delocalized units are being incorporated into polymeric structures.

The basic chemistry of osmium(II) is being developed. Other work has shown that πd electrons of Os(II) delocalize into π^* orbitals of unsaturated ligands even more rapidly than do those of Ru(II). Thus for Os(II) a wider choice of bridging unsaturated ligands leading to delocalization is possible than is the case for Ru(II).

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5. Nucleophilic Attack on Cyanoformate Induced by Co-ordination to Ruthenium Ammines, J. Chem. Soc. Chem. Comm., 622 (1974) Steven E. Diamond and Henry Taube.
6. Nitrogen-15-Labeled Complexes of $Ru(NH_3)_5N_2$, Inorg. Chem., 13, 479 (1974) S. Pell, R. H. Mann, H. Taube, N. Armor.

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62. CRYSTALLOGENICS, SURFACES, STRESS CORROSION CRACKING AND BIOMATERIALS

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Agency Support:

NSF-GA-41731
NSF-GH-33630 A3,4
NSF-DMR74-14650
NSF through CMR

Technical Objectives:

(a) To gain a complete and quantitative understanding of the crystallization process by controlling the state of chemical and physical perfection of crystals through control of the freezing process. The ultimate aim is the optimization and control of certain material properties.

(b) To theoretically analyze and experimentally investigate the various contributions which comprise the energy of both a stationary or moving interface between two phases plus how this energy changes with the detailed topography and chemical composition of the interface.

(c) To develop a quantitative predictive theory of corrosion events for gaseous, aqueous and liquid metal environments with the ultimate objective of controlling material properties to avoid cracking.

(d) To develop devices and techniques for monitoring properties of living systems.

Approach:

(a) Theoretical and experimental investigations of all the important elements of the crystallization process: nucleation, interface attachment kinetics, solute transport, fluid motion, interface morphology, physical imperfections and phase equilibria. The experiments are being carried out on a broad range of materials; e.g., stainless steels and other ferrous alloys, garnets, ice, etc., to elucidate the essential physics of the problem.

(b) The excess free energy associated with the interface is treated as a sum of five different parts: (i) a short-range quasi-chemical term due to changes in the orbitals of bound-electron states, (ii) a short-range transition structure term associated with the atomic diffuseness of the interfaces, (iii) a long-range electrostatic term associated with the equalization of the electrochemical potential of the electrons, (iv) a long-range strain term associated with the atomic displacements at the interface and (v) a chemical adsorption term associated with the redistribution of chemical species in the interface field due to (iii). Theoretical and experimental studies are being performed to determine Galvani potential differences between phases, chemical adsorption to surfaces and other factors needed in the evaluation of the accuracy of the theoretical analysis.

(c) A new approach to this important technological subject which utilizes basic understanding of surfaces on an atomistic level and treats the corrosion event (uniform or catastrophic) as a phase transformation. Theoretical models based on this approach allow experimental investigations of the effects of various parameters; e.g., surface energy, stress distribution, composition, grain boundaries and dislocations, etc.

(d) The approach is to develop reliable techniques for monitoring changes in the physiological state of living organisms--humans, animals and plants, via measurements on the external membrane. These changes in physiological state are associated with internal state changes and are registered as electrical, chemical, mechanical or other field variations at the membrane surface.

Significant New Research Directions:

(a) Theoretical crystallization studies are being conducted in the geological area. On a qualitative level, direct correlations are being made between observations and understanding of phenomena from metallurgical experience with those from geological experience. On a quantitative level, computations of crystallization velocity as a function of time and solute redistribution associated with this velocity profile are being carried out. The definition of laboratory experiments to test these computations are under way.

(b) The change in surface electrostatic potential for copper single crystals at ultra high vacuum under both homogeneous tensile and compressive stresses is being carried out experimentally. Previous studies in this laboratory with compressive stresses observed work function changes with elastic strain that were ~ 10^2 times the predicted theoretical value. Both elastic and plastic strains will be studied. Experiments will be extended to investigate specific inhomogeneous stress effects as well.

(c) Theoretical computations of inhomogeneous strain effects at surfaces have been made using a one-dimensional jellium model with short-range strain fields (~ 3-5 lattice spacings). The limitation to short-range strain fields occurs because of the use of a parameterized charge distribution rather than a self-consistent field method. The results show that inhomogeneous strain effects vs homogeneous strain effects are 5-10 times larger for the surface energy change and ~ 10^2 times larger for the work function change. In fact, a 10% surface tensile strain which decays to zero in 3 lattice spacings causes a surface energy lowering of 60%. For jellium alloys, extremely strong surface chemistry redistribution is expected to occur in response to inhomogeneous stresses so that for a 50-50 Rb-Cs alloy, the surface layer at 10% inhomogeneous tensile strain would be 100% Cs.

(d) The Kirlian photography studies are finally on an optimistic track. The key equations governing the discharge have been recognized and this allows effective applications design. The equations are (1) Kirchoff's current law for the entire circuit, (2) Paschen's law for the discharge gap and (3) continuity of electric flux at the membrane-air interface and at the film-air interface. It has been possible to explain why we did not see any dramatic physiological effects working at 100 kHz and 1 mHz. This is because the skin impedance is so small at these frequencies that insufficient voltage drop could be developed across the stratum corneum of human fingers to effectively modulate the overvoltage on the discharge gap. However, at ~ 1-10 kHz, both the impedance and the discharge current are greatly increased and the skin voltage drop is such that it does meaningfully modulate the discharge gap.

This means that Kirlian photography can now become a very effective tool for medicine, biology, agriculture, psychology, psychiatry and materials science.

Future Research Plans:

Continue all four areas of study with enhanced emphasis in the biomaterials area.

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63. BIOLOGICAL PHYSICS

M. Weissbluth, Associate Professor, Applied Physics

Graduate Students:

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S.C. Sheng

Agency Support:

NIH 1 R01AM17577-01

Technical Objective:

To obtain structural information on biological molecules by means of the EXAFS method.

Research Report:

This project employs a method known as EXAFS (Extended X-ray Absorption-edge Fine Structure) which is based on the characteristics of the X-ray absorption spectrum close to an absorption edge of a particular atom or ion. Synchrotron radiation emitted by 2-3 GeV electrons in a circulating storage ring at the Stanford Linear Accelerator Center (SLAC) serves as the X-ray source. Experiments have been performed on a number of porphyrins and on several varieties of hemoglobins.

Publications:

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64. FUNDAMENTAL STUDIES OF MAGNETIC MATERIALS

R. L. White, Professor, Electrical Engineering and Materials Science & Engineering

Graduate Students:

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C. H. Tsang
G. O. White

* Received Ph.D. during report period

Agency Support:

AROD	DAH-C04-72C-0014
NSF	through CMR
ONR	N0014-75-C-0290

Technical Objective:

To understand the macroscopic properties of magnetic materials in terms of the atomic properties of the constituents, and to design magnetic materials based on this knowledge.

Approach:

Spectroscopic studies, optical and microwave, are made on magnetic atoms or ions. The atomic level information thus obtained is used to explain the macroscopic magnetic properties of magnetic materials composed of these ions. Macroscopic magnetic properties are measured, when necessary, as well as related electrical parameters, such as Hall effect, when relevant. Crystals of interesting composition and properties are grown for exploration.

(1) New High Anisotropy Uniaxial Ferrimagnetic Oxides

Graduate Student: D. A. Herman, Jr.

The purpose of this project is to design new uniaxial magnetic materials, and in particular those which may show promise on bubble domain materials. We have selected for investigation copper ferrite, which we feel meets the above criteria. As it has developed, the difficult and time-consuming aspect of this project has been in the growing of single crystal stoichiometric $CuFe_2O_4$ and converting these crystals to the tetragonal phase.

Bubble domains have attained considerable recent prominence as potential memory devices. For a material to support bubble domains, it must display a uniaxial magnetic anisotropy of sufficient magnitude to overcome demagnetizing effects. If such is the case, a thin plate or film of magnetic material can be caused to magnetize normal to the plate if the plate is oriented perpendicular to the "easy" direction. The islands of reversed magnetization in such a plate are the "magnetic bubbles". A very limited number of materials have appropriate properties for supporting bubble; the leading "practical" bubble materials, the rare earth iron garnets, are not in fact intrinsically uniaxial but obtain their anisotropy from strain or growth artifact mechanisms. We have sought, therefore, an intrinsically uniaxial material of appropriate magnetic characteristics.

$CuFe_2O_4$ is one of the few ferrite spinels whose stable room temperature phase is tetragonal. The tetragonality is caused by a Jahn-Teller distortion of Cu^{2+} ions on octahedral sites. Essentially no data exist on the anisotropy of tetragonal $CuFe_2O_4$ because single crystals of tetragonal $CuFe_2O_4$ have never before been generated. Our efforts have, therefore, centered on synthesizing single crystal tetragonal $CuFe_2O_4$. We found that $CuFe_2O_4$ grown from flux at the usual growth temperature of 900 to 1000°C is copper deficient, sufficiently so that even after the appropriate annealing procedures to place the Cu^{2+} ions preferentially on the octahedral sites, not enough Cu^{2+} ions are on the octahedral sites to force a tetragonal phase. We have found that growth at a lower temperature, roughly 800°C, leads to more nearly stoichiometric $CuFe_2O_4$, and to a material which at room temperature is tetragonal on a microscopic level.

A Bi_2O_3-B_2O_3 flux system has been developed from which good quality bulk and epitaxial $CuFe_2O_4$ crystals can be grown.

The bulk crystals are very nearly stoichiometric and, when properly annealed, show the cooperative Jahn-Teller tetragonal distortion giving the c/a ratio of 1.06 typical of stoichiometric polycrystalline $CuFe_2O_4$.

Ferromagnetic resonance experiments were performed on single crystal spheres of $CuFe_2O_4$. The resonance spectrum indicated that the spheres were twinned in the sense that different portions of the crystal had selected different (100) cubic direction as the tetragonal c axis during the cubic to tetragonal transition. Examination of polished surfaces showed a characteristic twinning on 110 planes in a laminar fashion. To force systematic selection of a tetragonal c-axis thin crystals of $CuFe_2O_4$ were grown epitaxially upon single crystal spinel substrates. These epitaxial crystals were demonstrated by X-ray and by resonance data to be single crystal tetragonal, with the c-axis perpendicular to the substrate. Ferromagnetic resonance on annealed epitaxial films showed that $CuFe_2O_4$ has an "easy axis" form of uniaxial anisotropy, with $Ku \approx 1 \times 10^6$ ergs/cm^3. For the thin film $Ku > 4\ M^2$, so the film magnetizes spontaneously perpendicular to the plane of the film, meaning that $CuFe_2O_4$ is in fact a potential bubble domain material. Further crystal growth and experiments to produce bulk cyrstals of untwinned habit are in progress.

(2) Fundamental Limitations on Magnetic Domain Wall Velocities

Graduate Students: Geoff O. White
Ching Tsang

The data rate which can be achieved in bubble domain devices is limited by the rate at which magnetic bubbles can be run past a detection point. This rate is in turn determined by the domain wall velocity achievable, so the fundamental mechanisms limiting domain wall velocities have recently become of considerable interest.

For magnetic materials containing highly damped ions (coupled strongly) to the crystalline lattice) domain wall velocities and mobilites can be explained on a viscous damping picture. For low loss materials, like yttrium iron garnet, simple theory predicts domain wall mobilities two orders of magnitude higher than are experimentally observed. In the last two years, this discrepancy has largely been resolved, since theory has been developed which shows that the moving domain wall is subject to complex buckling and curling, leaving energy behind in what might be viewed as magnetic eddies. All these phenomena may be viewed also as spin wave instabilities in the simple wall structure, the canted antiferromagnetic orthoferrites, where all spin wave modes are of higher energy and hence harder to excite. Our study has two branches: (1) the measurement of domain wall velocities in $YFeO_3$, and (2) the characterization of the spin wave spectrum of a canted antiferromagnet by studying antiferromagnetic resonance in $NaMnF_3$. Both studies have proven very fruitful in recent months.

The domain wall velocity measurements have led to some remarkable results. Domain wall velocities versus drive field measurements have been made using a Sixtus and Tonks time-of-transit technique. In such a measurement a domain wall is nucleated at one end of a single crystal bar and its motion detected as it passes a number of coils spaced along the bar. Velocity measurements have been made for Bloch, Neél, and head-to-head domain walls, and over a temperature range from liquid N_2 temperature to roughly 400°C. For all three type walls domain wall velocities in excess of 10^6cm/sec have been observed (compared to maximum velocities on the order of 10^4cm/sec for garnets) and the domain wall velocity is linear in applied field for velocities up to 6 or 7 x 10^5 cm/sec. The mobility of the head-to-head walls is very high, approximately 50,000 cm/sec Oe at room temperature, and approximately an order of magnitude higher than the mobility of Bloch or Neél walls. All three types of walls interact magnetoelastically with sound waves when the wall velocity reaches the speed of sound. The interaction with transverse sound waves is stronger than with longitudinal sound waves, and is stronger for the head-to-head wall than for Bloch or Neél domain walls. Theoretical explanations for all these properties are being pursued.

The antiferromagnetic resonance spectrum of the canted antiferromagnet $NaMnF_3$ has been observed at frequencies in the range of 33 to 37 GigaHertz, at temperatures from 4.2°K to above the Neél temperature, 65°K, and in magnetic fields up to 20 K Gauss. This spectrum is of interest to the domain wall kinetics problem because it characterizes the spin wave spectrum to which the domain wall motion delivers energy through relaxation processes.

The canted antiferromagnet has, in zero applied field, two k = 0 antiferromagnetic resonance modes. The lower of these turns downward in frequency for an applied field along the principal spin direction. The upper mode turns upward in frequency for all directions of applied field. We have observed both modes at various temperatures and magnetic field orientations. From this data, plus static susceptibility and magnetization data, we are able to deduce the interaction parameters characterizing the magnetic behavior of the canted antiferromagnet and determining the spin wave spectrum of this material. The experimental portion of this study is essentially complete, and a good first order fit to the exchange (symmetric and antisymmetric) and anisotropy (orthorhombic) parameters obtained. A final adjustment of these parameters to compensate for polarization effects at high fields is now being pursued. When this fit is complete this project will have attained its primary goals and the spin wave spectrum so determined used in the domain wall damping calculations.

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SECTION C

PUBLICATIONS SINCE LAST REPORT

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SECTION D

DOCTORAL DISSERTATIONS

1. R. A. Armstrong, "Chemistry of Technetium in Low Oxidation States," Chemistry (January 1975).

2. P. V. Avotins, "Adsorption and Coprecipitation Studies of Mercury on Hydrous Iron Oxide," Applied Earth Sciences (June 1975).

3. R. F. Begley, "Higher Order Nonlinear Optics Processes in Solids and Liquids," Applied Physics (September 1974).

4. G. C. Bjorklund, "Vacuum Ultraviolet Holography," Applied PHysics (September 1974).

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6. B. Cabrera, "The Use of Superconducting Shields for Generating Ultra-Low Magnetic Field Regions and Several Related Experiments," Physics (April 1975).

7. H. N. Chang, "Studies on the Adhesion and the Aggregation of Blood Platelets," Chemical Engineering (April 1975).

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9. D. T. Cheung, "Properties of III-V Compound Heterojunctions Prepared by Liquid Phase Epitaxial Techniques," Electrical Engineering (June 1975).

10. S. S.-Y. Chiang, "Lattice Defects in Annealed Gallium Arsenide Single Crystals," Electrical Engineering (September 1974).

11. M. J. Clarke, "Purine Complexes of Ruthenium Ammines," Chemistry (September 1974).

12. L. L. Clements, "Deformation Behavior of High Density Polyethylene in Compression," Materials Science and Engineering (April 1975).

13. R. F. Cleverdon, "Configurational Thermodynamic Properties of Polar and Hydrogen Bonding Liquids," Chemical Engineering (June 1975).

14. J. Cogan, "The Creep of Weak Rocks in the Burgin Mine, Utah," Applied Earth Sciences (January 1975).

15. P. F. Coleman, "The Use of a Triphosphate Spin Label to Study Allosteric Equilibria in Abnormal Hemoglobins," Chemistry (September 1974).

16. J. L. Crowley, "Ionic Transport in Sulfonated Polystyrene Polyethylene Polyelectrolyte," Materials Science and Engineering (April 1975).

17. K. J. Czworniak, "A Molecular Interpretation of Mutual Diffusion Coefficients in Liquids and Their Measurement by Laser Light Scattering," Chemistry (June 1975).

18. D. H. Davis, "Investigation of One-dimensional Conducting Systems: Screening and Excitonic Superconductivity in Organo-metallic Compounds," Chemistry (September 1974).

19. R. J. DiMelfi, "Contributions to the Theory of Deformation and Fracture of Solids," Materials Science and Engineering (April 1975).

20. J. A. Dumesic, "Surface, Catalytic and Magnetic Properties of Small Iron Particles," Chemical Engineering (September 1974).

21. L. B. Ebert, "Characterization of Graphite Intercalated by Electron Acceptors," Chemistry (June 1975).

22. J. L. Falconer, "Flash Decomposition Spectroscopy Study of Formic Acid Decomposition on Clean Nickel (110)," Chemical Engineering (September 1974).

23. F. C. Fehrer, "Ultrasonic Hardening of OFHC Copper," Materials Science and Engineering (January 1975).

24. C. M. Fortunko, "Signal Processing with Surface Acoustic Wave Delay Lines," Applied Physics (June 1975).

25. R. R. Gagne, "The Binding of Oxygen in Hemoproteins; Model Fe(II) Systems Derived from 'Picket Fence' Porphyrins," Chemistry (September 1974).

26. T. W. Grudkowski, "Active Acoustic Waves and Electrons in Gallium Arsenide," Electrical Engineering (June 1975).

27. K. C. Harvey, "Doppler-Free Two-Photon Spectroscopy," Physics (June 1975).

28. D. A. Herman, Jr. "Crystal Growth and Magnetic Anisotropy of Copper Ferrite ($CuFe_2O_4$)," Electrical Engineering (April 1975).

29. I. C. Huseby, "The Mechanical Behavior of Magnesium Based Particulate Composites," Materials Science and Engineering (January 1975).

30. F. J. Kampas, "The Effect of Solvent Short-Range Order on the Solvent Sensitivity of Merocyanine Dyes," Physics (September 1974).

31. C. K. Kim, "Proton Enhanced Diffusion of Cadmium in Indium Antimonide," Electrical Engineering (September 1974).

32. B. M. Kincaid, "Synchrotron Radiation Studies of K-Edge X-Ray Photoabsorption Spectra; Theory and Experiment," Physics (June 1975).

33. M. N. Kronick, "Sensing of Structure-Specific Binding Onto Functionalized Quartz Surfaces Using Total Internal Reflection Fluorescence," Physics (September 1974).

34. C. G. Kuehn, "Chemistry of Ruthenium(II) Ammines with Hydrogen Sulfide and Other Simple Sulfur Ligands," Chemistry (January 1975).

35. R. W. Kugel, "Matrix Isolation Studies of Reactions of Atomic Oxygen with Sulfur Dioxide and Sulfur Trioxide," Chemistry (January 1975).

36. E.-H. Lee, "The Nucleation and Growth Kinetics of Gold on Mica Substrates," Materials Science and Engineering (January 1975).

37. R. A. Lemons, "Acoustic Microscopy by Mechanical Scanning," Applied Physics (June 1975).

38. A. W. L. Lin, Photoelectronic Properties of High-Resistivity GaAs:O and GaAs:Cr Single Crystals," Materials Science and Engineering (Minor: Electrical Engineering) (January 1975).

39. S. Lin, "Photoemission Studies of Thallous Chloride and Tetracyanoquinodimethane (TCNQ)-Based Organic Compounds," Applied Physics (Minor: Electrical Engineering) (January 1975).

40. C. M. Lyneis, "Experimental Studies of the Microwave Properties of 8.6 GHz Superconducting Niobium, Niobium-Tantalum, and Tantalum Cavities," Physics (September 1974).

41. R. J. Madon, "Gradientless Hydrogenation Kinetics in a Slurry Reactor," Chemical Engineering (April 1975).

42. J. G. McCarty, "An AES and Flash Desorption Study of Formic Acid Decomposition on Clean, Carburized, and Graphitized Ni(110)," Chemical Engineering (September 1974).

43. A. K. Miller, "A Unified Phenomenological Model for the Monotonic, Cyclic, and Creep Deformation of Strongly Work-Hardening Materials," Materials Science and Engineering (June 1975).

44. S. Narasimhan, "The Structure of Amorphous Alloys of Arsenic Triselenide and Thallium," Materials Science and Engineering (January 1975).

45. T. G. Ngo, "Effect of Platinum-Oxygen Interaction on the Catalyticity of Platinum for the Decomposition of NO_2," Chemical Engineering (January 1975).

46. S. J. Opella, "Carbon-13 Nuclear Magnetic Resonance Study of Muscle Calcium Binding Protein," Chemistry (January 1975).

47. H. J. Paik, "Analysis and Development of a Very Sensitive Low Temperature Gravitational Radiation Detector," Physics (January 1975).

48. G. G. Poe, "Closed Streamline Flows Past Rotating Particles: Inertia Effects, Lateral Migration, Heat Transfer," Chemical Engineering (April 1975).

49. P. Protopapas, "Derivation and Testing of a Statistical Mechanical Theory of Transport in Liquid Metals," Applied Earth Sciences (June 1975).

50. D. E. Post, Jr., "Electron Scattering from Organic Molecules," Physics (January 1975).

51. T. C. Reiley, "The Structure and Mechanical Properties of Physically Vapor Deposited Chromium," Materials Science and Engineering (January 1975).

52. C. G. Roberts, "Optically Scanned Acoustic Imaging," Applied Physics (September 1974).

53. J. D. Rodine, "Analysis of the Mobilization of Debris Flows," Geology (April 1975).

54. G. B. Rothbart, "An Experiment to Measure the Relative Velocities of Gamma Rays and Electrons at 15 GeV," Physics (April 1975).

55. R. T.-S. Shiah, "Photoconductivity of Amorphous V-VI, IV-V and IV-VI Semiconductors," Materials Science and Engineering (June 1975).

56. W. R. Shreve, "Parametric Interactions of Acoustic Rayleigh Waves," Applied Physics (September 1974).

57. J. W. Spencer, Jr., "Ultrasonic Velocities in Rocks Under Crustal Conditions," Geophysics (April 1975).

58. S. R. Stein, "The Superconducting-Cavity Stabilized Oscillator and an Experiment to Detect Time Variation of the Fundamental Constants," Physics (September 1974).

59. E. B. Stoneham, "The Effects of Ion-Implanted Gallium, Arsenic, and Phosphorus on the Diffusion of Ion-Implanted Zinc in Gallium Arsenide Phosphide," Applied Physics (June 1975).

60. B. D. Turnham, "The Physical and Chemical Adsorption of Nitric Oxide on Alumina and Other Oxides," Chemistry (January 1975).

61. M. T. Utine, "Extraction of Minor Elements from Todorokite (δ-MnO_2) and Associated Solid State Transformations," Applied Earth Sciences (January 1975).

62. L. R. Waterland, "Enzyme Immobilization Using Asymmetric Hollow Fiber Membranes," Chemical Engineering (June 1975).

63. D. M. Whitmore, "Multiple Scattering in Molecules With Applications to the Energy Band Structure of a Linear System," Physics (January 1975).

64. G. C. Wrighton, "Optical Properties of One-Dimensional Solids," Physics (September 1974).

65. S. H. Wu, "Lateral Phase Separations and Perpendicular Transport in Phospholipid Membranes," Chemistry (September 1974).

APPENDIX - I

I. FACULTY MEMBERS PARTICIPATING IN MATERIALS RESEARCH

Name	Title	Department(s)
A. Acrivos	Professor	Chemical Engineering
H. C. Anderson	Assoc. Professor	Chemistry
R. N. Anderson	Assoc. Professor	Applied Earth Sciences
B. A. Auld	Adjunct Professor	Hansen Laboratories
D. M. Barnett	Assoc. Professor	Materials Science & Engineering, Applied Mechanics
+C. R. Barrett	Assoc. Professor	Materials Science & Engineering
C. W. Bates, Jr.	Assoc. Professor	Materials Sciences & Engineering, Electrical Engineering
M. R. Beasley	Assoc. Professor	Applied Physics, Electrical Engineering
A. I. Bienenstock	Professor	Materials Science & Engineering, Applied Physics
M. Boudart	Professor	Chemical Engineering, Chemistry
J. I. Brauman	Professor	Chemistry
G. E. Brown	Asst. Professor	Geology
R. H. Bube	Professor	Materials Science & Engineering, Electrical Engineering
R. L. Byer	Assoc. Professor	Applied Physics
*J. P. Collman	Professor	Chemistry
T. J. Connolly	Professor	Mechanical Engineering
F. W. Dickson	Professor of Geochemistry	Geology
C. Djerassi	Professor	Chemistry
S. Doniach	Professor	Applied Physics
R. H. Eustis	Professor	Mechanical Engineering
C. W. F. Everitt	Adjunct Professor	Hansen Laboratories
W. M. Fairbank	Professor	Physics
M. D. Fayer	Asst. Professor	Chemistry

*CMR Executive Committee Member
+On Leave During Academic Year

P. J. Flory	Jackson-Wood Professor	Chemistry
H. O. Fuchs	Professor Emeritus	Mechanical Engineering
+*T. H. Geballe	Professor	Applied Physics, Materials Science & Engineering
J. F. Gibbons	Professor	Electrical Engineering
R. P. Giffard	Asst. Professor	Physics
S. S. Hanna	Professor	Physics
T. W. Hänsch	Assoc. Professor	Physics
S. E. Harris	Professor	Electrical Engineering
W. A. Harrison	Professor	Applied Physics
W. C. Hayes	Asst. Professor	Applied Mechanics, Surgery
*H. Heffner (Now deceased)	Professor	Applied Physics Electrical Engineering
G. Herrmann	Professor	Applied Mechanics, Civil Engineering
K. O. Hodgson	Asst. Professor	Chemistry
B. S. Hudson	Asst. Professor	Chemistry
*R. A. Huggins	Professor	Materials Science & Engineering
R. H. Jahns	Professor	Geology
A. M. Johnson	Assoc. Professor	Geology, Applied Earth Sciences
R. K. Kaul	Visiting Professor	Applied Mechanics
G. S. Kino	Professor	Electrical Engineering
E. H. Lee	Professor	Applied Mechanics, Aeronautics & Astronautics
J. E. Lind, Jr.	Assoc. Professor	Chemical Engineering
E. I. Lindau	Adjunct Professor	Hansen Laboratories
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D. M. Mason	Professor	Chemical Engineering Chemistry
H. M. McConnell	Professor	Chemistry

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D. A. Nagel, M.D.	Professor	Orthopaedic Surgery
*W. D. Nix	Professor	Materials Science & Engineering
+A. M. Nur	Assoc. Professor	Geophysics
R. H. Pantell	Professor	Electrical Engineering
G. A. Parks	Professor	Applied Earth Sciences, Geology, Environmental Engineering (Civil Engineering)
N. A. D. Parlee	Professor of Metallurgy	Applied Earth Sciences
+*G. L. Pearson	Professor Emeritus	Electrical Engineering
R. Pecora	Assoc. Professor	Chemistry
R. L. Piziali	Asst. Professor	Mechanical Engineering
G. M. Pound	Professor	Materials Science & Engineering
C. F. Quate	Professor	Applied Physics, Electrical Engineering
C. W. Richards	Professor	Civil Engineering
C. R. Robertson	Assoc. Professor	Chemical Engineering
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*D. A. Stevenson	Professor	Materials Science & Engineering
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H. Fischer	Chemistry
D. Franco	Chemistry
N. Fujii	Geophysics
C. W. M. Grant	Chemistry
H. R. Greenstein	Materials Science & Engineering
S. Gevorckjan	Applied Mechanics
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R. L. Herbst	Applied Physics
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C. F. Jako	Materials Science
J. S. Johannessen	Electrical Engineering
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APPENDIX - III

III. GRADUATE STUDENTS PARTICIPATING IN MATERIALS RESEARCH PROGRAMS

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P. Protopapas

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F. A. Gadala-Maria

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H. I. Lips
T. S. Lo

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S. A. Moese
S. R. Moosman
J. P. Muth

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T. G. Ngo
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V. M. Sanjana
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CHEMISTRY

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ELECTRICAL ENGINEERING

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D. M. Bloom
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L. N. Bui
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MATERIALS SCIENCE & ENGINEERING

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K. S. Majumder
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K. W. Mitchell
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J. C. Gibeling
C. D. Heising
D. V. Nelson
D. C. Rastegar
W. P. Seering
B. D. Sloane

APPENDIX - IV

IV. GRADUATE DEGREES CONFERRED

Doctor of Philosophy

R. A. Armstrong	Chemistry
P. V. Avotins	Applied Earth Sciences
R. F. Begley	Applied Physics
G. C. Bjorkland	Applied Physics
K. J. Bundy	Materials Science & Engineering
B. Cabrera	Physics
H. N. Chang	Chemical Engineering
V. W. C. Chang	Chemistry
D. T. Cheung	Electrical Engineering
S. Y. Chiang	Electrical Engineering
M. J. Clarke	Chemistry
L. L. Clements	Materials Science & Engineering
R. F. Cleverdon	Chemical Engineering
J. Cogan	Applied Earth Sciences
P. F. Coleman	Chemistry
J. L. Crowley	Materials Science & Engineering
K. J. Czworniak	Chemistry
D. H. Davis	Chemistry
R. J. DiMelfi	Materials Science & Engineering
J. A. Dumesic	Chemical Engineering
L. B. Ebert	Chemistry
J. L. Falconer	Chemical Engineering
F. C. Fehrer	Materials Science & Engineering
C. M. Fortunko	Applied Physics
R. R. Gagne	Chemistry
T. W. Grudkowski	Electrical Engineering
K. C. Harvey	Physics
D. A. Herman, Jr.	Electrical Engineering
I. C. Huseby	Materials Science & Engineering
F. J. Kampas	Physics
C. K. Kim	Electrical Engineering
B. M. Kincaid	Physics
M. N. Kronick	Physics
C. G. Kuehn	Chemistry
R. W. Kugel	Chemistry
E. H. Lee	Materials Science & Engineering
R. A. Lemons	Applied Physics
A. W. L. Lin	Materials Science & Engineering
S.-F. Lin	Applied Physics
C. M. Lyneis	Physics

Doctor of Philosophy (Continued)

R. J. Madon	Chemical Engineering
J. G. McCarty	Chemical Engineering
A. K. Miller	Materials Science & Engineering
S. Narasimhan	Materials Science & Engineering
T. G. Ngo	Chemical Engineering
S. J. Opella	Chemistry
H. J. Paik	Physics
G. G. Poe	Chemical Engineering
P. Protopapas	Applied Earth Sciences
D. E. Post, Jr.	Physics
T. C. Reiley	Materials Science & Engineering
C. G. Roberts	Applied Physics
J. D. Rodine	Geology
G. B. Rothbart	Physics
R. T.-S. Shiah	Materials Science & Engineering
W. R. Shreve	Applied Physics
J. W. Spencer, Jr.	Geophysics
S. R. Stein	Physics
E. B. Stoneham	Applied Physics
B. D. Turnham	Chemistry
M. T. Utine	Applied Earth Sciences
L. R. Waterland	Chemical Engineering
D. M. Whitmore	Physics
G. C. Wrighton	Physics
S. H. Wu	Chemistry

Engineer

C. J. Park	Materials Science & Engineering

GRADUATE DEGREES CONFERRED (Continued)

Master of Science

K. N. Bates	Applied Physics
S. J. Brosnan	Applied Physics
R. D. Caligiuri	Materials Science & Engineering
R. L. Champion	Electrical Engineering
B. A. Chin	Materials Science & Engineering
B. H. Coyle, Jr.	Applied Earth Sciences
G. R. Dodson	Materials Science & Engineering
F. W. Fitch	Geology
J. D. Fraser	Applied Physics
[illegible]. E. Gonzo	Chemical Engineering
G. L. Gussis	Chemical Engineering
S. Hahn	Materials Science & Engineering
D. F. Hoexter	Applied Earth Sciences
Y. W. Hu	Applied Physics
A. Kerdegari	Civil Engineering
J. S. Kim	Electrical Engineering
S. Lewkowitz	Materials Science & Engineering
D. T. Ling	Electrical Engineering
D. K. Misemer	Applied Physics
S. A. Moese	Chemical Engineering
S. R. Moosman	Chemical Engineering
E. H. Niccolls	Materials Science & Engineering
K. E. Norton	Materials Science & Engineering
J. C. Phillips	Applied Physics
M. S. Ritchie	Materials Science & Engineering
R. H. Roy III	Physics
B. D. Sloane	Mechanical Engineering
A. E. Soto	Applied Earth Sciences
J. E. Trummel	Applied Earth Sciences
B. Walser	Materials Science & Engineering
D. L. Weissman	Applied Physics
C. H.-C. Yuen	Physics

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